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LECTURE NOTES IN CHEMISTRY 1.

(*HARVARD COLLEGE.*)

DESCRIPTIVE CHEMISTRY.

ARRANGED BY

A. P. LOTHROP AND A. L. HODGES.

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DESCRIPTIVE CHEMISTRY.

Theoretical Chemistry. An *Element* is a substance which cannot by any known process be resolved into simpler substances. A *Compound* is a union of two or more substances, forming a new substance with new properties. A *Mixture* is a mechanical union of two or more substances, retaining the characteristic properties of each.

Law of Definite Proportions: Each compound contains the same elements in the same proportions.

Law of Multiple Proportions: When two compounds consist of the same elements, the proportion in one is a simple multiple of the proportion in the other.

HYDRIC PEROXIDE, H_2O_2, is formed by uniting baric peroxide and hydrochloric acid according to the following reaction:

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2.$$

Similarly we have the reaction of hydrochloric acid on baric oxide forming water:

$$BaO + 2HCl = BaCl_2 + H_2O.$$

These two reactions illustrate the law of multiple proportions. Hydric peroxide contains 2 parts by weight of H and 32 parts of O; while water contains 2 of H and 16 of O. *Properties:* hydric peroxide smells like chlorine and bleaches the skin. When concentrated as much as possible, it is of the consistency of syrup and freezes at — 30°. (Whenever in these notes degrees of temperature are mentioned, Centigrade is to be understood.) It is very unstable, readily giving up O, and is therefore a powerful oxidizer. Substances are attacked by the oxygen from it, when

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they are not attacked by O in a free state. This is due to the fact that the atoms in the molecule of free Oxygen (O_2) have a strong affinity for each other; but when O is just set free (nascent O), the two atoms have not yet combined and hence unite more easily with other substances. On this property depends its use in restoring pictures. The white lead of the picture, owing to the presence of sulphuretted hydrogen in the air, becomes in time converted into plumbic sulphide (black). By washing with hydric peroxide this is converted into plumbic sulphate (white).

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O.$$

Hydric peroxide also acts as a reducer, *i. e.* removes Oxygen, as from argentic oxide, thus leaving metallic silver.

$$Ag_2O + H_2O_2 = H_2O + Ag_2 + O_2.$$

Hydric peroxide is used for bleaching hair; it turns it to a greenish-yellow. "Golden Hair Water" is simply H_2O_2 in solution. Hydric peroxide in solution can be detected by adding to the liquid a little ether and a few drops of potassic dichromate. The H_2O_2 will form a perchromate soluble in ether, imparting to it a blue color.

The *Molecule* of *any substance* is the smallest amount of it that can exist in a free state.

The *Atom* of an *Element* is the smallest amount of it that occurs in any *Molecule*. In other words, when any substance is divided as far as possible by physical means, it is separated into molecules, which retain the qualities of the original substance. On carrying the division farther by chemical means, these molecules are split up into the atoms of the constituent elements. These definitions are a consequence of the *Atomic Theory*, which regards all substances as made up of atoms which unite to form molecules. The laws of definite and multiple proportions, which rest on experimental proof, are explained only by the assumption of some such theory as the atomic theory.

The determination of molecular weights depends on Avogadro's law: Equal volumes of all gases under the same conditions contain the same number of molecules. Hence the relative weights of these molecules must be the same as the relative weights of the equal gas volumes. By taking some one gas as the unit, all others can be referred to it. Since it is the lightest gas known, hydrogen is taken as the unit. The vapor density of a substance, therefore, is the weight of a volume of its gas referred to an equal volume of hydrogen gas; and the weight of the molecule of a substance referred to the hydrogen molecule is the same as the vapor density of that substance. But in determining molecular weights the hydrogen *atom* is taken as the unit. Since the H molecule contains 2 atoms, the molecular wt. of a substance $=$ its density $\times 2$. The weight of a molecule is of course equal to the sum of the weights of the constituent atoms.

The methods of determining atomic weight will be explained near the end of these notes.

There are three classes of reactions; analytical, synthetical, and metathetical. An *Analytical* reaction is when a compound breaks up into simpler substances, *e. g.*

$$2H_2O = 2H_2 + O_2. \quad \text{(Decompos. of water.)}$$

Decomposition is almost the only example of this class of reactions. A *Synthetical* reaction is when simpler substances unite to form a more complex, *e. g.*

$$2H_2 + O_2 = 2H_2O. \quad \text{(Combustion of hydrogen.)}$$

Combustion is almost the only case of this class. A *Metathetical* reaction consists in the interchange of radicals, *e. g.*

$$BaO + 2HCl = BaCl_2 + H_2O.$$

Metathetical reactions are by far the most common. *Stochiometry* is the branch of chemistry that treats of weights; for example, required the amount of $BaCl_2$ formed from 10g. of BaO. The reaction is given above.

$$\left.\begin{array}{l} \text{at. wt. Ba} = 137 \\ \text{'' '' O} = 16 \\ \text{'' '' Cl} = 35.5 \end{array}\right\} \qquad \begin{array}{l} BaO = 137 + 16 = 153 \\ BaCl_2 = 137 + 71 = 208 \end{array}$$

Forming a proportion, $153 : 208 = 10 :$ wt. required. If volume is required instead of weight, it must be remembered that

$$\text{volume} = \frac{\text{wt.}}{\text{sp. gr.}}$$

Berthollet's law: When two substances can form a substance insoluble or volatile under the conditions of the reaction, that insoluble or volatile substance will be formed till one of the factors is exhausted.

When the conditions of the law are not fulfilled, we shall have, besides the new substances formed, some of the original substances remaining uncombined.

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

The products being soluble, some NaCl and H_2SO_4 will remain uncombined.

A *Radical* is an atom, or any group of atoms that behaves like a single atom. Na is a simple radical; NH_4, a compound radical. A *Basic Radical* is a metal, or any radical that behaves like a metal. Na and NH_4 are both basic radicals. An *Acid* is a substance containing H which can be replaced by a basic radical. A *Salt* is formed from an acid by replacing its H by a basic radical. Thus in HCl, hydrochloric acid, the H can be replaced by Na, forming NaCl. An *Acid Salt* is a salt containing H that can be replaced by a basic radical. Thus in $NaHSO_4$, acid sodic sulphate, the H can be replaced by Na, forming Na_2SO_4. A *Hydrate* is formed from water by replacing one-half its H by a radical. A *Base*, or *Basic Hydrate*, is formed from water by replacing one half its H by a basic radical, *e. g.* water HOH, sodic hydrate NaOH. Bases have properties directly opposite to those of acids. An *Alkali* is a base soluble in water. An *Alkaline Earth* is a base only slightly soluble in water. The neutralization of an acid by a base or a base by an acid forms a salt, *e. g.*

$$NaOH + HCl = NaCl + H_2O.$$

The *Basicity of an Acid* is the number of atoms of H it contains which can be replaced by a basic radical. HCl is monobasic: Sulphuric acid, H_2SO_4, is di-basic, and can form both an acid and a neutral salt; Acetic acid, $HC_2H_3O_2$, is monobasic, as only one of its H atoms can be replaced. The *Quanticalence* of an atom or a radical is its combining capacity as measured by the number of H atoms which it will replace. Na is univalent, HCl,—NaCl; Ca is bivalent, 2HCl,—$CaCl_2$.

HYDROCLORIC ACID, HCl, is usually made by the action of sulphuric acid on common salt.

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

Properties: it is a strong acid, turning blue litmus paper red. It is a colorless gas, heavier than air, and fumes in moist air; very soluble in water, condensed by cold into a liquid. The acid dissolves some metals, giving up its H. Its salts are called chlorides.

Nitric Acid, HNO_3 can be formed by action of sulphuric acid on potassic nitrate.

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3.$$

But the commercial nitric acid is obtained from Sodic Nitrate.

$$2NaNO_3 + H_2SO_4 = 2HNO_3 + Na_2SO_4.$$

Properties: when pure, it is called *Fuming Nitric Acid* and is a colorless gas, very corrosive. It corrodes by giving up its oxygen, and is used as an oxidizer. It stains a bright yellow. It is soluble in water and the solution is usually yellow owing to impurities. It has a boiling point of 184°, and a specific gravity of 1.52. It dissolves Zinc, setting free H, which decomposes the acid so that we do not obtain free H. Its salts are called nitrates.

Sulphuric Acid, H_2SO_4, is made by burning sulphur, and then making the product take up more H and water. *Properties:* this is a strong acid and has a great affinity for water. When mixed with water, it gives out heat and precipitates an impurity, plumbic sulphate, which it takes up in preparation. Its salts are called sulphates.

Hydro-Sulphuric Acid or Sulphuretted Hydrogen, H_2S, is usually made from ferrous sulphide and sulphuric acid.

$$FeS + H_2SO_4 = H_2S + FeSO_4.$$

Properties: H_2S is a gas resembling HCl, with the odor of rotton eggs. It is poisonous when pure and in large quantities; harmless when mixed with air. It is slightly soluble in water and has a weak acid reaction, turning litmus paper a pinkish red. Its H cannot be replaced by Zinc unless the Zinc is in solution. It is a reducing agent and its salts are called sulphides.

The symbol of H_2S may be written in a graphical form, thus: H—S—H. The graphical symbol of H_2SO_4 is

$$\begin{matrix}\mathrm{H{-}O{-}}\\ \mathrm{H{-}O{-}}\end{matrix}\mathrm{S}\begin{matrix}=\mathrm{O}\\ =\mathrm{O}.\end{matrix}$$

This makes S sexivalent. Some chemists, however, maintain that the quantivalence of an element is always the same, whatever the compound in which it occurs. Thus, since S is bivalent in H_2S, they would make it bivalent in H_2SO_4, with the graphical symbol H—O—O—S—O—O—H. This view is probably incorrect.

WATER, H_2O, is the weakest of all acids, having no acid reaction with litmus paper. It forms acid salts, as $NaOH$; and neutral salts called oxides, as Na_2O.

CARBONIC ACID, H_2CO_3, is never obtained, since it breaks up into water and carbonic dioxide. Its existence is inferred from the existence of carbonates. The nearest approach to carbonic acid is soda water, a solution in water of carbonic dioxide. It has a weak acid reaction, and its H can be replaced by a basic radical, thus (theoretically):

$$H_2CO_3 + CaO_2H_2 = CaCO_3 + 2H_2O.$$

Carbonic dioxide or anhydride, CO_2, may be formed by the action of an acid on calcic carbonate (marble.) It is supposed that carbonic acid is first formed, which decomposes. CO_2 is heavier than air and will not support combustion. The salts of carbonic acid are called carbonates and may be formed by passing CO_2 through a solution of the soluble salt whose carbonate is required. They are usually formed however, by adding to the solution a soluble carbonate.

$$CaCl_2 + (NH_4)_2CO_3 = CaCO_3 + 2NH_4Cl.$$

The SILICIC ACIDS, H_2SiO_3 and H_4SiO_4, are unstable. Silicic Anhydride, SiO_2, is formed from H_2SiO_3. PHOSPHORIC ACID, H_3PO_4, forms three sodium salts, NaH_2PO_4, $NaHPO_4$ and Na_3PO_4. The word *anhydride* used above is a general term applied to substances which may be considered as formed from the acid by subtracting water.

Acids beginning with *hydro-* and ending in *-ic* and *-ous* contain H,O, and some third element which gives its name to the acid. The *-ic* acids have more O than the *-ous* acids. The *hydro*-acids form salts ending in *-ide;* those *-ic* acids which do not begin with *hydro-* form salts ending in *-ate; -ous* acids form salts ending in *-ite*.

AMMONIA GAS, NH_3, is produced by the decay of animal and vegetable matter containing nitrogen. It can be made artificially by distilling hoofs, horns, etc. (Hence the name hartshorn.) But it is usually obtained from ammonical liquor, *i. e.* the water through which coal gas has been passed to purify it. Water eagerly

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[ERRATUM. Line 26: should read "Acids beginning with *hydro-* contain H and some other one element. Acids not beginning with hydro- and ending in *-ic* and *-ous* contain," etc.]

absorbs ammonia, dissolving about 500 times its own bulk. The gas has a strong pungent odor. When hydrochloric acid and ammonia gas are brought together, a dense white cloud of solid ammonic chloride is formed.

$$NH_3 + HCl = NH_4Cl.$$

But this same substance is formed if the factors are in solution. The NH_4 corresponds to Na in NaCl and hence is a compound radical. The properties of the aqueous solution of ammonia gas resemble those of sodic hydrate, NaOH, and it acts like NaOH, forming with acids white crystallizable salts. Therefore it is probable that the solution is a true hydrate of the basic radical NH_4, and not a mere mixture.

AMMONIC CHLORIDE, NH_4Cl (sal ammoniac), is the most important of the ammonium compounds. To find the quantivalence of a compound radical, see how many bonds of the nucleus are left unsatisfied. Thus in the case of NH_4, since N is quinquivalent, NH_4 is univalent, because only 4 of the N bonds are satisfied by H. It is shown to be univalent by the compound NH_4Cl, since NH_4 replaces the atom H of HCl. *Properties:* soluble, colorless, neutral reaction, tastes like NaCl, but sharper. *Uses:* its most important use is as a source of the other ammonium compounds. It is also used as a drastic remedy, and in soldering to remove the coating of oxide which prevents the metals from uniting. It is obtained from ammoniacal liquor by the use of hydrochloric acid. Ammoniacal liquor contains as impurities, carbonic dioxide and sulphuretted hydrogen. These are driven off and then the solution is evaporated. It is heated to get rid of the tar, and the resulting mass is further purified by sublimation or crystalization. *Sublimation* consists in heating a volatile solid and condensing the vapor. The NH_4Cl purified in this way is in moderately flexible fibers. To purify by *Crystallization*, the substance is dissolved in water and then allowed to crystallize out.

AMMONIUM AMALGAM. A compound of NH_4 and mercury can easily be obtained by mixing NH_4Cl with an amalgam of mercury and sodium. A change takes place, resulting in the formation of common salt and an amalgam different from that put into the mixture. Something from the NH_4Cl has taken the place of the sodium in the amalgam. That something ought to be a metal, since nothing but a metal has ever been known to form an amalgam with mercury. It is therefore assumed by some that ammonium is a real metal with the molecule $(NH_4)_2$, resembling potassium, K_2.

$$Na_2 \text{ x } Hg + 2NH_4Cl = (NH_4)_2 \text{ x } Hg + 2NaCl.$$

The sodium amalgam, Na_2 x Hg, is formed by mixing sodium and hot mercury. The ammonium amalgam has the consistency of soft butter, and upon exposure to the air is broken up into mercury, nitrogen, and ammonia gas. Some chemists maintain that this is not a real amalgam but only a sort of suds. Their theory is supported by the fact that ammonia and hydrogen are squeezed out of it by pressure. The amalgam theory is supported by the fact that the froth formed freezes at a higher temperature than mercury, and that the hydrogen given off seems to be in a nascent state, which would hardly be the case were the substance merely a trough filled with ammonia and hydrogen.

Ammonic sulphydrate, NH_4SH, is made by passing sulphuretted hydrogen through ammonic hydrate.

$$NH_4OH + H_2S = NH_4SH + H_2O.$$

This is an acid salt of H_2S. The neutral salt is $(NH_4)_2S$, ammonic sulphide. Ammonic sulphydrate forms colorless crystals, which volatilize without decomposition; but when in solution, the sulphydrate is decomposed by the action of air. When decomposed, its color changes first to yellow and then to red. The change of color is owing to the formation of the sulphide, $(NH_4)_2S_2$.

$$8NH_4SH + 5O_2 = 2(NH_4)_2S_2 + 2(NH_4)_2S_2O_3 + 4H_2O.$$

When an acid is added to the sulphydrate, H_2S is evolved.

$$NH_4SH + HCl = H_2S + NH_4Cl.$$

If a part of the sulphydrate has decomposed, sulphur is also deposited.

$$(NH_4)_2S_2 + 2HCl = 2NH_4Cl + H_2S + S.$$

Ammonic sulphydrate has an alkaline reaction with test-paper (*i. e.* turns yellow turmeric paper red).

Ammonic sulphate, $(NH_4)_2SO_4$, is a neutral salt formed from ammonic hydrate and sulphuric acid. It is white, soluble, and has no reaction with test paper.

Ammonic carbonate is so unstable that it cannot be obtained pure, but from NH_4Cl and $CaCO_3$ we get the commercial carbonate, $NH_4HCO_3NH_4CO_2NH_2$, usually called smelling salts. This is colorless, pungent, soluble, with an alkaline reaction. By the action of air on smelling salts an acid carbonate is formed, which is white and soluble.

Ammonic nitrate, NH_4NO_3, is broken up by heat into water and nitrous oxide, N_2O (laughing gas). It is white and soluble, with a neutral reaction. All soluble salts of strong basic radicals with strong acids have neutral reactions; with weak acids, alkaline reactions.

Sodium Na. At. wt. 23. This is a metal: it is one of the most important and widely diffused of the elements, occurring in many rocks, sea-weeds, and beach-plants. The chief source of it is common salt.

Salt, NaCl, is found in solid beds. In the salt mines at Wielizka, in Austrian Poland, it occurs in such large quantities that subterranean chapels are hewn from it. In Cheshire, England, it is found in the form of boulders, and only needs to be ground. Where it cannot be found sufficiently pure, advantage is taken of its solubility, and wells are sunk, as at Syracuse, N. Y. These consist of two tubes, an outer and an inner. The inner tube extends further down than the outer, and has at the bottom a cap perforated with small holes. Water is poured down the outer tube to dissolve the salt. The weight of this water forces the brine part way up the inner tube; it is then pumped up the rest of the way. Some salt-wells are from 3000 to 4000 ft. deep. In some countries, as in Germany, natural salt-springs occur. The brine from wells and springs is usually placed in tanks and evaporated by the sun; but in Germany where the springs are dilute the brine is first concentrated in a *graduation frame*. This is a frame filled with fagots over which the brine trickles. The wind to which the frame is exposed evaporates water, and causes salts less soluble than common salt to be deposited on the fagots. The concentrated brine is then evaporated by heat. In countries where the sun is very hot, salt is also obtained from sea water, which contains

2.7%. It is evaporated in *salt-gardens* or *salinas*. The water is led into a series of tanks each shallower than the preceding. In the first the insoluble impurities are deposited; in the second, salts less soluble than NaCl; in the third, NaCl, which is called Bay Salt. The liquid remaining contains salts more soluble than NaCl, and is called Bittern. *Properties:* salt is a white substance, soluble about equally in hot and cold water, with a neutral reaction. Salt crystallizes in cubes, which are frequently grouped together in the shape of hoppers near the surface of the liquid. Salt crystals are apt to decrepitate, that is, burst when heated. This is due to water enclosed mechanically between the plates of the crystals, and not to water of crystallization. *Uses:* the chief use is in making sodic carbonate. It is also used in making salt glaze [see Pottery under Aluminum] and as an antiseptic.

SODIC SULPHATE, Na_2SO_4, usually crystalizes with $10H_2O$, and is then called Glauber salts. The first stage in the manufacture of sodic carbonate from NaCl is the conversion of NaCl into Na_2SO_4.

$$2NaCl + H_2SO_4 = NaHSO_4 + NaCl + HCl.$$
$$= Na_2SO_4 + 2HCl.$$

The mixture of NaCl and H_2SO_4 is put into a reverberatory furnace, away from the fire, where the first reaction takes place, forming the acid sulphate. The solid mass is then raked out on the hearth of the furnace where the flame will approach nearer to it. Here the second reaction takes place and the neutral sulphate called *salt cake* is formed. The HCl from the reactions passes up through towers packed with coke, over which water trickles. The water absorbs the HCl, forming a crude solution of HCl (the muriatic acid of commerce). *Properties:* if we dissolve the salt cake, we obtain crystals containing 10 molecules of water called water of crystallization. If we allow the crystals to remain in the air at ordinary temperatures, the water is given up and the salt crumbles into powder. Salts that lose their water of crystallization in this way at ordinary temperatures are called *Efflorescent*. Salts that absorb water from the air and dissolve in this water are called *Deliquescent*, as zincic chloride. Salts that neither absorb nor give up water at ordinary temperatures are called *Permanent* salts. Sodic sulphate is white, with a neutral reaction. Its solubility in water increases with the temperature up to 28° and then decreases. It can form a supersaturated solution. A *Saturated* solution of a salt is one that contains as much of the salt as it can hold. A *Supersaturated* solution is formed by dissolving at a high temperature as much of the salt as the water will take up. It is then placed in a flask, corked tightly, and allowed to cool. The surplus salt is not precipitated and the solution is called supersaturated. But as soon as the flask is uncorked or jarred, the salt crystallizes out, leaving the solution saturated. *Uses:* sodic sulphate is used as a drastic remedy. A solution of the crystallized salt in hydrochloric acid is accompanied by considerable depression of temperature and hence is used as a freezing mixture.

SODIC CARBONATE, Na_2CO_3, usually crystallizes with $10H_2O$ and is then called sal soda. This was formerly obtained in England from the ashes of some sea-weeds, as Kelp and Varec; in Spain from the ashes of beach plants, and was then called Barilla. During the French Revolution the supply of barilla from Spain was cut off, and a prize was offered for the discovery of a process of manufacturing the carbonate from common salt. A French chemist named Le Blanc discovered the process now so largely used. Its manufacture is probably the greatest chemical industry in the world except the manufacture of sulphuric acid. Le Blanc's process consists first in converting the NaCl into Na_2SO_4, as described above. The salt-cake is then heated in a reverberatory furnace with powdered coal and limestone ($CaCO_3$). The reaction is in two stages.

$$\begin{aligned} Na_2SO_4 + 2C + CaCO_3 &= 2CO_2 + Na_2S + CaCO_3. \\ &= Na_2CO_3 + CaS + 2CO_2. \end{aligned}$$

The black mass then raked out is called *black ash* or *ball soda*. It must be separated from CaS by *lixiviation*. This consists in treating the black ash with water. The sodic carbonate dissolves out, leaving behind the insoluble impurities. By evaporating this solution the impure carbonate called *soda ash* is obtained. This is then redissolved and allowed to crystallize, forming fine crystals of sal soda. *Properties:* sal soda is colorless, soluble, efflorescent, with an alkaline reaction. It is used in making glass. [See glass under Silicon.]

ACID SODIC CARBONATE, $NaHCO_3$, is usually called saleratus. To make an acid salt we can add to the neutral salt another molecule of the acid.

$$Na_2CO_3 + H_2CO_3 = 2NaHCO_3.$$

Since carbonic acid cannot be obtained, the acid carbonate is usually prepared by passing carbonic dioxide through a vessel in which crystals of sal soda have been placed. The crystals lose their water of crystallization, one molecule of which passes into the new compound.

$$Na_2CO_3 10H_2O + CO_2 = 2NaHCO_3 + 9H_2O.$$

Properties: it is soluble and feebly alkaline. When it is mixed with an acid, a violent effervescence ensues, caused by the escape of CO_2. With a given amount of acid, twice as much CO_2 is obtained by using the acid carbonate as by using the neutral carbonate.

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2.$$
$$2NaHCO_3 + 2HCl = 2NaCl + 2H_2O + 2CO_2.$$

Upon this property depends its chief use, that of bread-raising. The object of raising bread is to make it more digestible; it is made more porous, and thereby a larger surface is offered to the action of the gastric juice. The best method of raising bread is by the use of yeast. This is a plant related to mold. When it is mixed with dough, it converts the starch into sugar, and then into CO_2 and alcohol. Fermentation is thus produced in the dough. The yeast plant is destroyed in baking, the form of the mass is fixed, and the alcohol driven off. Saleratus is used as a substitute for yeast. When it is mixed with an acid, CO_2 is given off. The acids used are sour milk (lactic acid), Cream of Tartar, (tartaric acid), and Horsford's Baking Powders (calcic superphosphate). The use of these is injurious, as an insoluble salt is formed and deposited in the bread. The salt formed by using cream of tartar is sodic potassic tartrate or Rochelle salts. The symbol of cream of tartar may be represented by $HK\overline{T}$, where $\overline{T}$ represents a complex formula.

$$NaHCO_3 + HK\overline{T} = NaK\overline{T} + H_2O + CO_2.$$

Horsford's yeast powder was introduced to restore the phosphate removed from the flour by bolting. It puts in very much more than the bolting removes. Saleratus is also used in soda powders (as Rochelle or Sedlitz powders) for making effervescing drinks. The other ingredient of the powders is some acid or acid salt.

SODIUM, Na_2, was first obtained by Sir Humphrey Davy in 1807. It is prepared by heating sodic carbonate with powdered charcoal to a white heat in an iron retort.

$$Na_2CO_3 + 2C = Na_2 + 3CO.$$

The sodium volatilizes and the vapor passes out with the CO into a copper receiver. The upper part of the receiver is surrounded by a wire basket filled with ice. In this receiver the vapor of the metal is condensed, while the gas escapes through an opening near the top. The condensed metal falls into mineral naphtha to prevent oxidation. *Properties:* sodium is white, with a metallic lustre, can be moulded by the fingers, and is lighter than water. It oxidizes very easily, so that it has to be kept in naptha. If exposed to air the oxide formed absorbs water and is converted into sodic hydrate. When it is thrown upon water the water is decomposed.

$$Na_2 + 2H_2O = 2NaOH + H_2.$$

The reaction is accompanied by the evolution of heat, which, if the sodium is not free to move about, is so great as to set fire to the hydrogen. The flame is yellow owing to the presence of volatilized particles of sodium. *Uses:* sodium is used in extracting gold from its ore. If the ore contains sulphur, a weak sodium amalgam will act upon it more readily than mercury alone. Sodium is also used in the preparation of aluminum, and the hydrate is an important laboratory reagent.

SODIC HYDRATE, NaOH (caustic soda), is formed by the action of water on sodium. The hydrate thus formed is very pure, but is so expensive that it is only used in delicate chemical processes. The ordinary hydrate is obtained from sodic carbonate and calcic hydrate.

$$Na_2CO_3 + CaO_2H_2 = 2NaOH + CaCO_3.$$

This reaction takes place because $CaCO_3$ is insoluble, and whenever an insoluble carbonate can be formed it is formed. *Properties:* sodic hydrate is white, fusible, soluble, caustic, with an alkaline reaction. *Uses:* it is used in the arts as a cheap alkali. The principal use is in the manufacture of soap. This is made by boiling sodic hydrate with fat. Fat is a mixture of ethers or organic salts, each composed of a basic radical C_3H_5 (glyceril, trivalent) and an acid. These acids are three in number, stearic, palmitic, and oleic. Since stearic acid enters most largely into the composition of fats, we may regard fat as a stearate of glyceril, $C_3H_5\bar{S}_3$ (where $\bar{S}$ represents a complex formula). On boiling, the following reaction takes place:

$C_3H_5\bar{S}_3 + 3NaOH = C_3H_5O_3H_3$ (glycerine) $+ 3Na\bar{S}$ (sodic stearate, soap).

The mixture of fats and lye is boiled in vats called "coppers" usually, however, made of iron. Then it is put into brine and the soap is precipitated, while the glycerine remains in solution. Palm oil soap, however, is soluble is salt water, and hence can be used for washing in sea water. Castile soap was originally made in Spain with the hydrate obtained from barilla. The red streaks were due to iron in the barilla. Now white castile soap is made from the hydrate of pure sodic carbonate obtained by Le Blanc's process. To satisfy consumers who were suspicious of the white castile soap, manufacturers added iron to the soap, thus making artificial red streaks. Before Le Blanc's time sodic hydrate was so expensive that potassic hydrate was used in making soap, forming potassic stearate. By adding NaCl this was converted to sodic stearate. While Na makes hard soap, K makes soft soap. Calcic stearate, formed when soap is used with hard water, is insoluble, as is also plumbic stearate. Plumbic stearate or Lead soap, is used, under the name of Lead plaster, in surgery, to hold together the edges of wounds.

SODIC NITRATE, $NaNO_3$, is the only compound of sodium not formed from the carbonate or the chloride. It occurs native in Peru, and in Atacama, Chili, whence it is sometimes called Chili saltpetre. The pure salt crystallizes in rhombohedra and is very soluble in water. It is used for making nitric acid and potassic nitrate. It is slightly deliquescent, and therefore cannot be used in the manufacture of gunpowder. It has a neutral reaction.

The test for sodium is a bright yellow flame when heated in the Bunsen lamp, and a yellow band in the spectroscope. In the spectrum $\frac{1}{3000000}$ mgr. of sodium can be detected.

Potassium, K, At. wt. 39.1. Although potassium is not found anywhere in such large quantities as sodium is, yet in small quantities it occurs almost universally in rocks. The mica and felspar of quartz contain potassium. Where rocks containing potassium are disintegrated by the air, the soluble potassium salts are set free and work into the soil. These salts are taken up by plants and the potassium is stored up in their tissue. All soils that do not contain potassium are sterile, and when this has been removed by vegetation, it must be restored by manure or by letting the land lie fallow.

POTASSIC CARBONATE, K_2CO_3. It is obtained: (1) from the ashes of the leaves and small stems of many plants and of herbs by lixiviation. The product thus obtained is called potash. A purer potassic carbonate called pearlash is obtained by burning and lixiviating potash. Potash is brought from the Canada backwoods, Hungary, and Prussia. That this method of obtaining potassic carbonate from wood ashes may be profitable, wood must be cheap. It must be remembered that the ashes of land plants give potassic carbonate, while those of sea and beach plants give sodic carbonate. (2) The molasses of beet-root sugar is evaporated and burned, and potash is lixiviated out. (3) From the KCl in the Stassfurth salts K_2CO_3 is obtained by Le Blanc's process [see under Sodic Carbonate]. (4) K_2CO_3 is obtained from suint or sheep-sweat, by evaporating the wool washings and then burning and lixiviating the residue. Of these sources of potassic carbonate (1) and (3) are the most important. *Properties:* it resembles Na_2CO_3, except that it is deliquescent while Na_2CO_3 is efflorescent. *Uses:* it is used as a source of potassic hydrate, KOH, from which soft soap is made, and also as a source of the acid potassic carbonate. These resemble the corresponding sodium compounds and are often used in place of them.

POTASSIUM, K_2, is extracted from the carbonate in the same way as sodium. It resembles sodium, but has a slight pinkish tinge and is acted upon by air and water more violently than sodium is. While sodium must be kept in one place on the surface of water in order to burn, potassium bursts into a violent flame even when in motion. Potassium is about six times as costly as sodium.

Potassic chloride, KCl, is one of the most important K salts. The chief source of it is the Abraum salts of Stassfurth. These occupy the site of an ancient sea which has evaporated, depositing its NaCl and other salts in the order of their solubility. It is found at Kalusz in Galicia in large crystals called sylvine. KCl is also obtained by the evaporation of bittern. The Abraum salts containing K are dissolved and concentrated by evaporation. The KCl crystallizes out, leaving the more soluble salts in solution. *Properties:* it resembles NaCl, but it is much more soluble in hot than in cold water, while NaCl is about equally soluble in each. It is white, has a neutral reaction, and crystallizes in cubes with octahedral modifications. It is used in the manufacture of potassic carbonate by Le Blanc's process.

Potassic sulphate, K_2SO_4, is anhydrous, *i. e.* crystallizes with no water of crystallization. It is less soluble than sodic sulphate. It is used as a manure to restore potassium, usually with magnesic sulphate.

Potassic nitrate, KNO_3, called also nitre or saltpetre is very important. (Nitrogen, nitre-maker, is named from this.) Potassic nitrate occurs as an efflorescence on the surface of the soil in certain hot countries, as in India. It occurs also in Hungary, where it is obtained by lixiviating the earthen floors of peasants' huts. For its formation, an alkaline soil that has much animal matter, and sufficient porosity for the O of the air to have access, is necessary. In Sweden the process of nature is imitated in the nitre plantations. Heaps of animal matter rich in N (hides, hoofs, etc.), wood ashes containing K_2CO, slaked lime, and earth are set up. Straw is added to keep the mass porous. The heap is terraced, except on one side, which is left vertical. This is directed towards the prevailing wind of the country. It is protected from the rain by a roof, but the air has free access. The heap is washed every day with liquid manure. Calcic nitrate, $Ca(NO_3)_2$, is formed in the heap, and by a sort of capillary action is deposited in the strip of earth next the vertical side. This is removed about every two years, lixiviated with K_2CO_3, and the lixiviated earth is put back on the terraced sides. In the process of lixiviating with K_2CO_3 the following reaction takes place:

$$K_2CO_3 + Ca(NO_3)_2 = CaCO_3 + 2KNO_3.$$

This is called the splitting of nitre. The chemical process of the formation of nitre in the nitre heaps is as follows: animal matter gives off ammonia, consisting of N and H. These unite with the O of the air to form H_2O and HNO_3. Then the HNO_3 acts on the CaO_2H_2, thus forming $Ca(NO_3)_2$. The nitre must now be purified to remove the deliquescent salts and other impurities. For this purpose it is dissolved in a copper kettle heated at the sides and bottom. Consequently currents of heated liquid rise at the side, cool at the top, flow towards the middle, and there sink. A pot is hung in the middle of the kettle, and in this the insoluble impurities collect. The purified solution is run off into pans and allowed to crystallize. During crystallization it is constantly stirred to prevent the formation of large crystals, and so nitre meal is formed. The reason of this is that the large crystals would imprison in them some of the mother liquor containing the soluble impurities. The chief of these impurities is salt; and since salt is nearly as soluble in cold as in hot water, while nitre is much less soluble in cold than in hot water, the salt remains in solution with the mother liquor, while the nitre crystallizes out. It is then washed to get rid of the mother liquor till the wash water gives no test for NaCl. Nitre may also be obtained from sodic nitrate by potassic chloride.

$$NaNO_3 + KCl = KNO_3 + NaCl.$$

Properties: nitre crystallizes in thick, flat plates with bevelled edges. It is white, soluble, and has a neutral reaction. On being heated, nitre first fuses and then gives up one atom of O.

$$KNO_3 = KNO_2 + O.$$

If heated still further, it parts with another atom of O and lastly with its N. On this depends its property, when heated with carbon and sulphur, of deflagration, *i. e.* quick, sparkling combustion without explosion. *Uses:* nitre is used with NaCl for preserving meat, as an oxidizer and antiseptic, and as a medicine; also in making HNO_3 [see under HNO_3]. When cotton is soaked in strong nitric acid and then dried, it forms a violent explosive called gun-cotton. An important use of KNO_3 is in the manufacture of gunpowder. *Gunpowder* is a mixture of nitre, carbon and sulphur, in the proportion of about 75 parts nitre, 13 carbon, and 11 sulphur. Sulphur is used because it is easy to ignite, while the function of the carbon is to retain the spark. The object of the nitre is to furnish O to the S and C, so that the powder will burn in an enclosed space. The explosion is due to the fact that the powder is resolved into a mixture of gases occupying 1500 times the original space. These gases are chiefly CO_2 and N_2, but also to a small extent CO, H_2, H_2S, O_2. Solid products are also formed, chiefly K_2SO_4 and K_2CO_3, but also $K_2S_2O_3$, K_2S, KSCN, KNO_2, C, S, $(NH_4)_2CO_3$. The discovery that these compounds are formed is due to Bunsen. The C is obtained by heating wood, chiefly buckthorn and willow, in iron cylinders; small twigs and bark are rejected since they contain K_2CO_3 (deliquescent), which would spoil the powder. The nitre is in the form of nitre meal, and the sulphur in the form of roll-brimstone. The three ingredients are pulverized and thoroughly mixed. For this there are two methods, known as the stamp process and the drum process. In the *Stamp Process* the substances are placed in bronze mortars and beaten with bronze pestles. In the *Drum Process* they are placed in revolving drums or cylinders containing bronze bullets called edgestones. When thoroughly mixed they are kneaded with water and pressed by a hydraulic press into a solid mass called Press-cake. This is then granulated in parchment sieves with wooden discs. The grains are polished in a revolving drum by friction against one another. The reason that press-cake cannot be used without granulation is that it is too compact for a spark to pass through it easily, and hence only a part of it would ignite. Meal powder, on the other hand, would ignite too easily; by its too rapid explosion time would not be given to overcome the inertia of the ball and the gun would burst. For common powder, where a longer time is required to overcome the enertia of the ball, coarser grains must be used. In the Krupp guns hexagonal prisms, perforated, are used. The characteristics of good gunpowder are these: color, slate gray or brownish; grains, of uniform size; lustrous; should not soil the hands; nor break between the fingers; when burned upon paper should not blacken it much. For blasting, a powder more violently explosive is needed, so that time will not be given for it to overcome the inertia of the tamping; hence a larger proportion of S is used. In the manufacture of gunpowder for fireworks, potassic chlorate is sometimes used instead of nitre. Colored fires consist of gunpowder colored by some salt; sodium salts give yellow, lithium salts red. The stars of rockets and Roman-candles are gunpowder mixed with iron filings to cause sparkling. The *test for potassium* is a violet flame, giving a red band in the spectroscope. It also forms a yellow chlorplatinate, K_2PtCl_6.

Lithium, Li, at. wt. 7, is one of the most common of the rare elements. It is widely diffused, though in small quantities. We know that it occurs in the soil, for Li_2CO_3 is found in the ashes of many plants, as tobacco. This absorption of Li from the soil makes tobacco very destructive to the soil. Li is also found in a few rare minerals, as Lepidolite and Spodumene. Li is the lightest metal known, and floats on naphtha. Sp. gr. 0.5. It has to be kept from the air to prevent oxidation, and closely resembles Na and K; but the carbonate and the phosphate of Li are only sparingly soluble in water, while the corresponding Na and K salts are soluble. The flame of Li salts is a beautiful crimson, giving a red band in the spectroscope. This is a very delicate test; .000009 mgr. may be thus detected.

Rubidium, Rb, at. wt. 85.4, and **Caesium**, Cs, at. wt. 133, are among the rarest of the elements. They were discovered by Bunsen by means of the spectroscope. Caesium has been found in the Durkheim springs in Germany. Lepidolite contains about .02% of Cs. The mineral Pollux was analyzed by a German chemist, who supposed it to be a silicate of potassium. But the per cents would not add up 100; the mineral was afterwards discovered to be a silicate of a new metal, Caesium. Rb. and Cs resemble K, but their Pt compounds are less soluble than those of K.

The metals hitherto treated form the first group of metals, known as the *alkaline metals*. We shall now take up the metals composing the second group, known as the *alkaline earths*. Metals of the first group are univalent, those of the second group bivalent; compounds of the first group are soluble almost without exception.

those of the second group are nearly all insoluble; the hydrates of the first group are readily soluble and cannot be decomposed by ignition, those of the second group are sparingly soluble and can be decomposed by ignition.

Calcium, Ca, at. wt. 40, is more abundant than even Na or K.

CALCIC CARBONATE, $CaCO_3$, or CALCITE, is the most important mineral containing Ca, and next to quartz it is the most abundant of all minerals. When crystallized in rhombohedric crystals it forms Iceland spar; when in sharp tooth-shaped crystals, it is called Dog's-tooth spar. Iceland spar has the property of double refraction and polarizes light. Marble is a more compact calcite, crystallized or uncrystallized. When pure, it is white, but it is often colored by various impurities. Chalk is the fossilized shells of animalculae. Limestone is rougher and more impure than marble. When we want pure $CaCO_3$ we make it chemically or use Iceland spar.

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$$

Calcic carbonate is insoluble in water but soluble in H_2CO_3. When therefore water containing CO_2 meets limestone in its path, it dissolves a part of it, forming *temporarily hard water*. When the CO_2 escapes, $CaCO_3$ is precipitated. Thus spring water trickling through the roofs of caves loses its CO_2 and deposits calcite in the form of stalactites pendant from the roof. The water falling on the floor before it has parted with all its CO_2 makes a deposit of calcic carbonate called a stalagmite. Fossils and petrifactions are formed like stalactites by the loss of CO_2. When a substance is merely covered with $CaCO_3$, it forms a petrifaction; when it is thoroughly converted to stone, it forms a fossil. Deposits of $CaCO_3$ from streams and lakes form, when loose, Tufa; when compact, Travertine, which was used by the Romans for building purposes. Calcic carbonate occurs in the secretions of many animals, as coral, and in shells; also in bones. *Properties*: the carbonate is white, insoluble in water, and said to be soluble in acids; but this is not strictly true. In reality, when a substance is said to be soluble in acids, a chemical reaction takes place and a new soluble compound is formed; *e. g.*

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

$CaCO_3$ when heated gives off CO_2. When the CO_2 is unable to escape (as in a gun barrel) the carbonate fuses, solidifies, and makes white statuary marble. It is supposed that the statuary marble in the earth's crust was thus formed. *Uses:* it is used in sculpture (marble), and in drawing (chalk), as a flux in separating iron from its ores, and in making glass. It is also used in making Na_2CO_3 by Le Blanc's process, and for lithographic stones. These are a compact variety of limestone, on which the design is drawn in a greasy ink. The stone is then moistened with water, and a roller covered with greasy printing ink is passed over it. This ink adheres only to the design, which being greasy does not retain the water. Impressions are then taken of the design. Chromos are only colored lithographs, and a separate stone is required for each color. Chalk is used in fireworks to give an orange yellow color to the flame.

Calcic Oxide, CaO (Quicklime), is prepared by heating in a limekiln calcic carbonate, usually in the form of travertine.

$$CaCO_3 = CaO + CO_2.$$

There are two kinds of limekilns; the continuous, and the intermittent. At the base of the continuous kiln there is a door for removing the oxide, while the carbonate is put in at the top; the fire is at the sides. In the continuous kiln an arch made of lumps of limestone is formed over the fire grate. The kiln is then filled with smaller fragments, and a fire built. After three days' and three nights' burning, the lime is removed. *Uses:* quicklime will not fuse even in the oxyhydrogen blowpipe; hence it is used in the lime light, and in crucibles in which platinum is fused. It has a great affinity for water, so that it is used as a dehydrater, *e. g.* if added to dilute alcohol, it unites with the water, forming a solid, calcic hydrate, and the alcohol can then be distilled off.

Calcic Hydrate, CaO_2H_2 (slaked lime), is formed by the action of water on quicklime. This is the process known as the Slaking of Lime.

$$CaO + H_2O = CaO_2H_2.$$

This, like all synthetical reactions, is accompanied by the evolution of heat. *Properties:* slaked lime is a white powder, slightly soluble in water, with an alkaline reaction. A solution of it in water is called lime-water. If CO_2 be added to lime-water, $CaCO_3$, is precipitated. This is the usual test for Co_2. By adding more lime, milk of lime, or whitewash, is formed; by adding still more a paste of lime is formed. *Uses:* paste of lime mixed with sand and water forms mortar. The sand is used to give coherence to the mortar by furnishing points to which the particles may attach themselves as they harden. The hardening of mortar is due to these causes: (1) the evaporation of water; (2) absorption of CO_2 from the air, converting superficially at least, calcic hydrate to calcic carbonate; (3) the action of calcic hydrate on the sand, forming calcic silicate (very hard).

$$SiO_2 + CaO_2H_2 = CaSiO_3 + H_2O.$$

Ordinary mortar will not harden under water. But silicate and phosphate of aluminum will; so limestone is used, containing one or both of these substances, or else they are added in the form of clay to the pure limestone in the limekiln; such cements are called hydraulic cements. The most important of these is Portland cement, so called because of its resemblance to Portland stone. Calcic hydrate is used as a manure to set free the ammonia from animal matter, and in making NH_4OH and $NaOH$. From its property of taking up acids it removes H_2S from coal gas; it removes hair from hides in tanning, is used in dyeing and bleaching as an alkali, and to remove some impurities from sugar.

CALCIC CHLORIDE, $CaCl_2$, is soluble and the most deliquescent substance known. Owing to its great attraction for water it is one of the best drying agents. To dry gases we pass them through a succession of U-tubes filled with $CaCl_2$. To dry a liquid, $CaCl_2$ is put into it and then the liquid is distilled off. To dry a solid, put it with $CaCl_2$ into a closed box. The $CaCl_2$ absorbs water from the air, and this in turn takes it from the solid. $CaCl_2$ is also used in organic analysis. The substance to be analyzed is burned, and the hydrogen unites with the oxygen of the air to form water. This is absorbed by the $CaCl_2$ and thus the amount of hydrogen in the original substance can be known. $CaCl_2$ with snow, produces sufficient cold to freeze mercury. In trying to combine with water it melts the snow very rapidly, thus absorbing a great amount of heat. The molecule of crystallized $CaCl_2$ contains $6H_2O$.

Calcic Sulphate, $CaSO_4$, is usually found as gypsum or alabaster. When crystallized it contains $2H_2O$. It is white and soft. Gypsum has three cleavages; the principal cleavage splits it into thin plates, and the other two into rhombs. It is slightly soluble and hence occurs in almost all spring water. Hard water is water containing salts of Ca or other soluble salts. The most common is that containing $CaSO_4$, forming *permanently hard water.* Soap will not dissolve in hard water, but is precipitated as calcic stearate.

$$2Na\bar{S} + CaSO_4 = Ca\bar{S}_2 + Na_2SO_4 .$$

This lime soap has no cleansing effect. There is no easy way of removing $CaSO_4$ from permanently hard water, but temporarily hard water can be rendered soft by adding slaked lime.

$$H_2CO_3 + CaO_2H_2 = CaCO_3 + 2H_2O.$$

Upon the removal of the CO_2 from the water, the $CaCO_3$ previously in solution is precipitated along with that just formed. The degree of hardness of water can be determined in this way: a standard solution of soap is made and put in a tube having a graduated scale. The solution is then added to a given volume of the water to be tested, until the calcic stearate is all precipitated and a suds begins to be formed. The amount of the solution used can then be read off from the scale, and thus the degree of hardness of the water determined. When temporarily or permanently hard water is used in a boiler, the sulphate or carbonate is precipitated, forming *boiler scale.* The precipitation of the sulphate is due to the fact that its solubility decreases as the temperature rises. The disadvantages of boiler scale are these: (1) It is expensive, since it is a poor conductor of heat, and more fuel must be used to heat the water. (2) Owing to the different rates of expansion of the boiler scale and the boiler, the scale splits, and the water coming in contact with the red-hot iron is suddenly turned to steam, thus causing an explosion. (3) The iron of the boiler gets heated since it is unprotected by the water, and is liable to burn through. There are two ways to prevent boiler scale. The *mechanical* method consists in putting into the water some rough article, as bran or sawdust, upon which the $CaSO_4$ collects. The *chemical* method consists in adding to the water some substance that will unite chemically with the $CaSO_4$, sal ammoniac for instance.

$$CaSO_4 + 2NH_4Cl = CaCl_2 + (NH_4)_2SO_4.$$

Besides the soap test for the hardness of water, there is another called the alcohol test. $CaSO_4$ is less soluble in alcohol than in water; so if we add alcohol to permanently hard water, $CaSO_4$ is precipitated. $CaSO_4$ is soluble in HCl and has a neutral reaction. Its crystals are small and indistinct. One of the most important of its properties is the action of heat upon it. Heat drives off the $2H_2O$ and leaves anhydrous $CaSO_4$, called Plaster of Paris. This name is given to it since large quantities of gypsum are found in the neighborhood of Paris. Plaster of Paris has the property of reabsorbing water, becoming gypsum. It expands into a solid mass, thus taking the exact shape of the vessel or mould. In taking casts, it is mixed with water to the consistency of cream and poured into a mould, hardening in a few minutes. To take a cast of a statue, a shell of plaster is formed around it and when dry removed from the statue in sections. The hollow shell is put together again and plaster of Paris poured in. When a coating has been formed on the sides of the mould, the liquid plaster is poured out and a hollow cast is formed. Stucco is a mixture of plaster and glue, which hardens more slowly than plaster alone, and takes a high polish. Encaustic is a mixture of plaster and soap. The soap gives it a lustre like marble. Gypsum is porous and is used as a manure. It is also used as a paper-filling, and, under the name of terra alba, to adulterate confectionery. In these last cases it is used simply to add weight.

CALCIC NITRATE, CaN_2O_6, is formed in the nitre-plantations. It is a deliquescent salt, soluble in alcohol.

For CHLORIDE OF LIME, CaOCl, see under Chlorine.

The metal CALCIUM, Ca_2, is a mere curiosity and has to be kept under naphtha.

Strontium, Sr, at. wt. 87.6, and barium are not so common as calcium, but yet are not rare. Strontium occurs in nature as a sulphate, $SrSO_4$, called celestine (because sometimes blue), and as a carbonate, $SrCO_3$, called Strontianite. Strontianite was discovered in 1787 at Strontian in Argyleshire and was then regarded as baric carbonate. Hope, in 1791, and Klaproth, in 1793, discovered that this mineral contained a peculiar earth, and Sir Humphrey Davy, in 1808, first obtained from it the metal strontium. Salts of strontium, especially the nitrate, are used in making cheap red fire.

Barium, Ba, at. wt. 137, occurs in nature as the sulphate, $BaSO_4$, called barite or heavy-spar (βαρύς), and as a carbonate called witherite. Baric sulphide, BaS, was known as early as the seventeenth century, under the name of Bologna phosphorus, so called because when exposed to the light and then carried into a dark room it became luminous or phosphorescent. The element barium was first recognized as distinct from calcium by Scheele, in 1774, but was not isolated until 1808, by Sir Humphrey Davy.

BARIC CHLORIDE, $BaCl_2$, one of the most important compounds of barium, may be prepared from the carbonate by HCl; but since the carbonate is very rare, it is usually made from the sulphate. The sulphate is reduced by heating with charcoal, and the residue, BaS, is treated with HCl.

$$BaSO_4 + 2C = BaS + 2CO_2.$$
$$BaS + 2HCl = BaCl_2 + H_2S.$$

The principal use of $BaCl_2$ is in testing for sulphuric acid or sulphates.

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl.$$

The $BaSO_4$ is in the form of a white precipitate insoluble in dilute HCl + aq. $BaSO_4$ is soluble in strong HCl. On adding $BaCl_2$ to other acids precipitates are formed, but these are soluble in dilute HCl.

BARIC NITRATE, BaN_2O_6, is used like $BaCl_2$ in testing for sulphuric acid. It is sometimes used instead of KNO_3 in blasting powder (saxifragine).

BARIC HYDRATE, BaO_2H_2, is made by heating baric sulphide and cupric oxide.

$$BaS + CuO + H_2O = BaO_2H_2 + CuS.$$

It crystallizes in flat plates like strontic hydrate. Calcic hydrate, however, crystallizes with difficulty. Notice that the solubility of the hydrates of Ba, Sr, and Ca, varies inversely with the atomic weights of the elements. [See table on p. 31.]

BARIC SULPHATE, $BaSO_4$, is insoluble in water and in dilute acids. Consequently it can be used as a white paint, called "permanent white" because it is not discolored by H_2S in the air. It is also used as a paper-filling, especially in paper collars. Barium gives a green flame and green bands in the spectroscope.

Magnesium, Mg, at. wt. 24. is nearly as abundant as Ca, and quite as abundant as Na and K. It is found in large quantities in magnesian limestone called Dolomite, a magnesio-calcic carbonate $(MgCa)CO_3$, or x $MgCO_3$ y$CaCO_3$. This mixture resembles calcite. Mg also occurs native in the form of the hydrous silicates talc or tailor's chalk, soapstone, serpentine (used for ornamental purposes) and meerschaum. Another source is the anhydrous silicates, hornblende and asbestos. Hornblende is a constituent of syenite, taking the place of the mica of ordinary granite. Asbestos is a fibrous hornblende, and can be made into cloth. It is incombustible and hence is used for roofing. It is a poor conductor of heat and is therefore used for surrounding steam-pipes. Another source of Mg is magnesite, a white mineral, which is not very common, but which occurs largely in Euboea. Lastly, Mg is obtained from the Abraum salts of Stassfurth. Salts of Mg occur here associated with salts of K.

MAGNESIC SULPHATE, $MgSO_47H_2O$, is called Epsom salts, because found in the mineral springs of Epsom. It is very soluble and therefore remains in the mother liquor of NaCl after partial evaporation of the sea-water. To this mother liquor it gives the name bittern from its bitter taste. It is used as a manure with K_2SO_4, and also as a medicine. It is found in such large quantities that other uses are sought for it. $MgSO_47H_2O$ forms with $(NH_4)_2SO_4$ a double salt $MgSO_4(NH_4)_2SO_46H_2O$. It forms this by replacing one molecule of water with the $(NH_4)_2SO_4$. A similar salt can be formed with K_2SO_4.

MAGNESIC CHLORIDE, $MgCl_2$, is obtained from the waste products of the Stassfurth potash-works. It crystallizes with $6H_2O$ and is very deliquescent. Although very abundant, no uses of much importance have as yet been found for it. At present it is used for watering streets, moistening yarn, as a disinfectant, and as a fire extinguisher. When heated with water it is decomposed.

$$MgCl_2 + H_2O = MgO + 2HCl.$$

Since we cannot obtain an anhydrous $MgCl_2$ by evaporating the solution, we take advantage of the fact that it will form a double chloride of ammonium and magnesium, $MgCl_2NH_4Cl$. By heat, the ammonic chloride is driven off, and anhydrous magnesic chloride remains.

Magnesium, Mg (probably), is obtained from $MgCl_2$ by heating it with sodium.

$$MgCl_2 + Na_2 = Mg + 2NaCl.$$

Mg is like Zn in most of its qualities. At ordinary temperatures it is rather more brittle than silver, but is malleable at a temperature a little below redness. Volatilizes at about the same temperature as Zinc. It is a whitish metal, not so blue as zinc, and is slightly tarnished by the air, but unlike Ca, Sr, and Ba it does not have to be kept in naphtha. It is very light, having a sp. gr. of 1.74. It is very combustible, giving a brilliant white light accompanied by dense clouds of white smoke, MgO.

$$2Mg + O_2 = 2MgO.$$

It is not used on any large scale for lighting purposes because the smoke is disagreeable and it is very expensive, costing about twenty-five times as much as gas. The only establishment for the manufacture of magnesium is at Manchester, England. Its only important use thus far is for magic lanterns. To insure continuous combustion the metal must be kept in contact with the flame. To accomplish this, lamps are provided with clockwork for pushing into the flame the magnesium wire or tape. The same purpose is effected by blowing magnesium dust into the flame. It has been proposed to use magnesium for light-houses and signals.

Magnesic oxide, MgO, can be obtained by burning Mg, but this is expensive. It is usually obtained by heating magnesite.

$$MgCO_3 = MgO + CO_2.$$

It can also be obtained by heating the nitrate, but made in this way it is heavier than when made from the carbonate. *Uses:* it is sometimes used in the oxy-hydrogen light in the place of lime, giving a more brilliant light. It slakes like CaO, forming MgO_2H_2; but unlike CaO it changes from a powdery form to a solid lump in the process.

$$MgO + H_2O = MgO_2H_2.$$

Upon this last property depends its use in making artificial stone and emery wheels. Emery wheels were formerly made by cutting them out of the solid rock; but now powdered emery is mixed with MgO. The mixture is moistened and put into a mould; the hydrate thus formed sets and cements the emery powder. In making artificial stone the oxide is mixed with the powder of the stone to be imitated, and moistened. It can then be made into blocks of any form desired. The manufacture of artificial stone has proved a failure, since the magnesic oxide is too expensive; so the artificial-stone factories have been turned into emery-wheel factories. There is one at Malden, Mass. One of the best ways of taking geological casts is by means of magnesic oxide. *Magnesic hydrate*, MgO_2H_2, is slightly soluble in water and so we get an alkaline reaction, substances insoluble of course giving no reaction.

MAGNESIA ALBA, $xMgO_2H_2\ yMgCO_3$. Here x and y represent a variable number of molecules. Magnesia alba is a basic salt. A *Basic salt* is a double salt which contains the hydrate of an element and some salt of the element. Magnesia alba is formed by adding sodic, ammonic, or potassic carbonate to some soluble magnesic salt, as the sulphate.

$$2MgSO_4 + 2Na_2CO_3 + H_2O = 2MgCO_3 + 2Na_2SO_4 + H_2O.$$
$$= MgO_2H_2MgCO_3 + 2Na_2SO_4 + CO_2.$$

But it is also made from Dolomite by passing CO_2 through water containing powdered Dolomite in suspension.

$$MgCO_3CaCO_3 + H_2O + CO_2 = MgH_2(CO_3)_2 + CaCO_3.$$

The CO_2 in solution dissolves the $MgCO_3$ from the $CaCO_3$, forming the acid carbonate. This, being in solution, can be removed from the insoluble $CaCO_3$. The solution, forming magnesian temporarily hard water, on being boiled loses CO_2 and precipitates the carbonate mixed with the hydrate, that is, magnesia alba.

$$2MgH_2(CO_3)_2 = MgCO_3MgO_2H_2 + H_2O + 3CO_2.$$

The relative proportion of the hydrate and the carbonate varies. Magnesia alba is very light and porous. It will remove grease spots by absorbing the grease in its pores, is used as a medicine and as a source of other Mg salts. Salts of Mg when fused in the blow-

	Mg.	Ca.	Sr.	Ba.
METALS,	Permanent.	Naptha.	Naptha.	Naptha.
OXIDES,	MgO.	CaO, CaO_2.	SrO, SrO_2.	BaO, BaO_2.
HYDRATES,	Nearly insoluble. Alkaline, not caustic.	Slightly soluble, more alkaline, caustic.	More soluble, alkaline and caustic.	Soluble, very alkaline, very caustic, poisonous.
CHLORIDES,	Deliquescent. $MgCl_2 + H_2O = MgO + 2HCl$. Double NH_4 salts.	Deliquescent. Not decomposed by H_2O. None.	Slightly deliquescent. Not decomp. by H_2O. None.	Not deliquescent. Not decomp. by H_2O. None.
	$6H_2O$.	$6H_2O$, $2H_2O$.	$6H_2O$.	$2H_2O$.
SULPHATES,	Soluble. $7H_2O$.	Slightly soluble. $2H_2O$.	Almost insoluble. Anhydrous.	Insoluble. Anhydrous.

pipe with cobaltous nitrate give a pink color; this is a test for Mg. *Resemblances between Ca and Mg:* Both are bivalent; each forms but one series of salts; their salts from strong acids have neutral reactions; their carbonates crystallize in the same form. *Differences:* It is hard to get magnesic carbonate pure from the hydrate, easy to get calcic carbonate pure; Mg forms but one oxide, Ca, two. For other differences see table.

Zinc, Zn, at. wt. 65.2, is not so abundant as Ca or Mg, but next to iron is the most abundant of the useful metals. Brass, an alloy of Zn, was known to the ancients, but they used an ore of Zn and not the pure metal. The alchemist Paracelsus, in the 16th century, mentions Zn, but the element was not extracted in Europe till the 18th century. Zn is found in a neutral locality between Germany and Belgium, in New Jersey, and in Somersetshire, England. The chief ores are *Calamine*, a silicate, Zn_2SiO_4 $2H_2O$, *Smithsonite*, $ZnCO_3$, and *Blende*, ZnS. Blende when pure is white, but it is usually black from the presence of iron. It is crystalline, with a waxy lustre. There are two other ores: Franklinite, which is found only in America, and occurs in black octahedra; and red oxide, which is found in great abundance in New Jersey. *Extraction of Zinc.* The process of extracting a metal from its ores is called Metallurgy. The process here consists (1) in converting the ore to the oxide; (2) in reducing the oxide to the metal. In the extraction of Zn, if the ore be Smithsonite or calamine, the oxide may be obtained directly by heating the ore.

$$ZnCO_3 = ZnO + CO_2 . \quad Zn_2SiO_4 = 2ZnO + SiO_2 .$$

Blende must be roasted to burn off the sulphur.

$$2ZnS + 3O_2 = 2ZnO + 2SO_2 .$$

In this country the ore is usually roasted in open piles, while in Belgium a conical kiln is used. The oxide thus formed is red from the iron in it. Since nearly all metals occur either as oxides or as sulphides, the principal branches of metallurgy are the reduction of sulphides and the reduction of oxides. The oxide is reduced by heating it with carbon, which has a stronger attraction for O than Zn has.

$$2ZnO + C = 2Zn + CO_2 .$$

The oxide contains iron and gangue; but when reduced, the Zn is volatilized by the heat and passes off, leaving behind the non-volatile impurities. For reduction there are three processes: the Belgian, the Silesian, and the English. In the *Belgian Process* cylindrical retorts are used, which are packed in a furnace on ledges of masonry and incline downward towards the front. These retorts are made of clay, and to each retort is fitted a short conical condenser made of earthenware. To these first condensers in turn are fitted sheet iron conical condensers (second condensers). The retorts are so packed that the condensers extend outside. The powdered oxide mixed with coal dust is put into the retort. Since there are some volatile impurities, the second condenser is not at first put on, and the gases are allowed to escape through an opening at the end of the first condenser. Cadmium usually occurs with Zn, and, since it is more volatile than Zn, distills off first. By the brown color of its smoke it is known when the Cd is all driven off. When the smoke becomes white, the second condenser is put on. While the iron condenser still remains cold, Zn falls in powder. When the condenser grows hot, the Zn melts but will not flow out since there is a bend in the condenser. There is an opening at the end of the second condenser to allow the CO_2 formed to escape; otherwise it would burst. *Silesian Process.* In Germany a muffle-shaped earthen retort is used, which has a curved condensing tube fitting into an aperture near the top and leading downward. The volatilized Zn is condensed in this tube and flows out into a receptacle at the bottom. The tube is liable to become clogged and has to be cleared from time to time through an opening in the bend. In the Belgian process the ores can be graduated to the amount of heat required for each, that is, the harder ores can be placed nearer the fire. In the Silesian process this is impossible, since the retorts are all at the same distance from the fire. The *English Process* is very inferior. The condenser leads downward from the bottom of the retort. It is one of the few cases in which distillation downward is still practised. The distilled metal passes down partly in powder and partly in fused masses. The rough Zn obtained by these methods is remelted and cast into ingots. *Properties:* Zn is a bluish white metal, only slightly tarnished by air, with crystalline structure as seen on fracturing it. Between 100° and 150° Zn is malleable, but above and below these temperatures, brittle. It melts at 412°, and when volatilized burns with a greenish flame. Sp. gr. varies from 7.03 to 7.2. It resembles Mg in many of its properties, forms white compounds, has but one oxide and its chloride is decomposed by water and heat. *Uses:* Zn rusts upon the surface when exposed to air, forming a basic carbonate which protects it from further action. Hence it is used to cover the roofs of houses and the bottoms of ships. It expands on cooling and therefore gives good casts; hence it is sometimes used for statues. On account of its lustre it is used for gas fixtures and for ornamental purposes. Pieces of Zn cut in facets are used for stage diamonds, and at a little distance can hardly be distinguished from the real. Granulated zinc is made by dropping melted zinc into cold water. Zinc is also used in the electric battery for generating an electric current. By placing two plates, one of zinc and the other of platinum, in a vessel containing sulphuric acid, and connecting the plates, a current passes from one to the other through the connecting medium. The zinc plate is called the negative, and the platinum the positive pole. At the same time the zinc is dissolved and hydrogen appears on the platinum plate. The theory of this is that the SO_4 in one molecule of H_2SO_4 unites with an atom of zinc, forming $ZnSO_4$, while the hydrogen set free combines with the SO_4 in the next molecule of H_2SO_4, driving the hydrogen of this to a third, and so on. The hydrogen in the molecules of H_2SO_4 next the platinum plate collects on the surface of the platinum; so in a short time the plate becomes covered with hydrogen and the battery ceases to act. There are two methods of preventing this coating of hydrogen. The *mechanical method* consists in making the platinum plate as rough as possible and perforated, so that it does not become so soon covered. This device is used in *Smee's cell.* The *chemical method* is by using a *Bunsen* or a *Grove cell.* In each case the cell consists of a vessel in which is placed sulphuric acid and a hollow cylinder of amalgamated zinc. The zinc is amalgamated so that when the battery is at rest, the sulphuric acid will not act upon it; but when the zinc is connected with the platinum, the amalgam does not stop the action of the sulphuric acid. Within this cylinder of zinc is placed a cylindrical vessel of porous earthenware filled with strong nitric acid, in which is placed a plate of platinum (Grove cell) or gas carbon (Bunsen cell). The pores in the earthenware vessel are too small to let acid pass through, but are large enough to let the molecules of hydrogen pass through. This free hydrogen combining with the oxygen in the nitric acid to form water is thus prevented from reaching the inactive carbon or platinum plate. (The least soluble plate is called the inactive plate.) Such a battery does not last long, for the nitric acid finally becomes so much diluted that it does not act on the free hydrogen, which therefore reaches the platinum and carbon. This battery gives off disagreeable fumes, owing to NO_2 and N_2O_3 set free; hence a solution of chromic anhydride is often used in the place of nitric acid. Zinc is used because it is the cheapest of the easily soluble metals. Iron is not very soluble in acids. The strength of the current depends on the *difference in solubility* between the active and the inactive plates. If iron is used instead of platinum for the inactive plate, a weaker current is developed and no iron dissolves until all the zinc is used up. It is upon this fact that the use of zinc in galvanized iron depends. The article to be galvanized is thoroughly cleansed and dipped into melted zinc. Thus the core is pure iron, the outside pure zinc, and between these there is an alloy of zinc and iron. By the action of the air a thin layer of the basic carbonate is formed upon the zinc, which prevents any further action of the air. If, however, the zinc be worn off in any place, a battery is formed between the iron and the zinc through the moisture and acids in the air. The iron cannot be touched by the air till all the zinc is worn away, because, being the inactive plate, it is covered by a layer of hydrogen. The zinc itself dissolves much faster than it would if the battery were not formed. So when iron nails are used to fasten on zinc plates, as to the bottom of a ship, a battery is formed, dissolving the zinc rapidly around the nails, so that the plates fall off. Impure zinc is much more soluble in acids than pure, since it forms a battery by itself with its impurity (usually iron). Zinc is used to prevent the corrosion of steam boilers by the water containing air and acid salts. Bars of zinc are hung in the water and a battery is formed with the sides of the boiler. Hydrogen is usually made from zinc. Zinc has one important alloy, brass, made by melting together copper and zinc.

Zincic oxide, ZnO, may be formed by burning Zn in the air.

$$2Zn + O_2 = 2ZnO.$$

An impure oxide, tutty, is formed in large quantities in the flues of chimneys of brass factories. ZnO known as "zinc white" is used as a pigment. It is superior to white lead, in that it is not blackened by H_2S in the atmosphere, but, although like $BaSO_4$ it is permanently white, it does not combine chemically with the oil, and hence easily peels off. ZnO turns yellow when heated, but this color leaves on cooling. The name "nihil album" was given to it by the alchemists. It is used as a medicine.

Zincic sulphide, ZnS, is white. It is formed from a soluble salt of Zn by means of $(NH_4)_2S$.

$$ZnCl_2 + (NH_4)_2S = ZnS + 2NH_4Cl.$$

It is soluble in acids, insoluble in water. This is the first striking difference between Mg and Zn.

Zincic chloride, $ZnCl_2$, butter of zinc, is white, deliquescent, soluble in H_2O and alcohol. It has great attraction for water and is therefore used as a disinfectant and antiseptic. There is an oxychloride of Zn which is used for filling teeth; it sets in a white mass. A double chloride of zinc and ammonium is used as a solder solution to remove the film of oxide from the metals. $ZnCl_2$ cannot be obtained from its solution by evaporation, as it decomposes, forming the oxide.

$$ZnCl_2 + H_2O = 2HCl + ZnO.$$

In this it resembles $MgCl_2$.

Zincic sulphate, $ZnSO_47H_2O$ (white vitriol) is white and resembles $MgSO_4$ in its properties. All sulphates that crystallize with $7H_2O$ form double sulphates; *e. g.* $ZnSO_4(NH_4)_2SO_46H_2O$ and $MgSO_4(NH_4)_2SO_46H_2O$. Zincic sulphate is soluble, with an acid reaction, and is used in medicine. Zincic hydrate is precipitated from a solution of a salt of Zn by $NaOH$ or KOH, but is dissolved by an excess of the alkali.

Cadmium, Cd, at. wt. 112, occurs with Zn in its ores and is obtained from the ore when Zn is extracted. [See extraction of Zn.] Cadmium is one of the commonest of the rare elements. The only important ore of Cd is CdS, Greenockite. The metal is closely related to Zn and in a less degree to Mg. Its melting pt. is 242°. It is very volatile and hence its vapor density can easily be determined. Its sp. gr. is 8.6. When bent it emits a grating sound like tin. This is called its "cry" and is caused by the crystalline plates rubbing against one another. The metal has one use; it makes a fusible alloy. Its compounds are all white, except CdO, which is brown, and CdS, which is yellow. The sulphide is insoluble in water and acids; difference from Zn. It is the only compound of much importance and is used as a yellow paint. It is the best of that color. The bromide, $CdBr_2$, and the iodide, CdI_2, are pearly white and used occasionally in photography.

Indium, In, and **Gallium**, Ga, are very rare, Ga especially. They occur associated with Zn, and being about as volatile as Zn, come over with it in distillation. They were discovered by means of the spectroscope; In in 1863, Ga in 1876. Ga was discovered by Le Cocq-Boisbandran, a Frenchman, just after the close of the Franco-Prussian war, and its name was given it as a hit at Germany.

Aluminum, Al, at. wt. 27., is about as abundant as Ca. It occurs in many precious stones, as sapphire (blue) which is Al_2O_3, and in some Oriental gems, as the Oriental ruby (red), emerald (green), topaz (yellow), amethyst (violet), garnet (dark red), and turquoise (opaque blue). Emery is impure Al_2O_3, containing some ferric oxide. Most rocks and soils contain Al. Felspar and mica both have more Al than K. Clay is a hydrous silicate of Al and slate is a hardened clay.

POTTERY. The art of making pottery was known very early. Pottery is found even in the remains of the bronze age, and nearly all savages are acquainted with it. The ancient Egyptians made pottery images. The Romans, Greeks, and Etruscans carried the art to a high degree of development. During the Middle Ages pottery disappeared, but the art was refound at the time of the

Renaissance by the Moors in the Balearic Islands. Pottery was introduced into Italy under the name of *Majolica*, from the name of the island Majorca. The usual colors of Majolica are blue and yellow. Palissy ware was named from its inventor, Palissy. He had spent all his money in his experiments and was just about tearing down his house to obtain fuel. His wife was on the point of having him shut up as a lunatic, when he discovered the long sought for art. Majolica and Palissy ware, when genuine, are worth their weight in gold.

Pottery may be divided into two classes; ware with a fused base and ware with a porous base.

WARE WITH A FUSED BASE. *Porcelain* was originally brought from China and Japan, where the art has been known from the earliest times. All attempts to imitate the ware were for a long time unsuccessful, because real porcelain clay could not be obtained; but at last, in 1710, it was discovered by Böttger, an alchemist who was trying to solve the secret of the philosopher's stone in order to redeem himself from captivity in Dresden. In his experiments he had made ware with a partly fused base, and now in the hair-powder of his barber he accidentally found the material for the ware, porcelain clay or kaolin. A manufactory was set up at Meissen and the workmen kept under close surveillance. But notwithstanding this, one escaped and carried the secret to Vienna, where a factory was soon established. From these they soon spread, and the porcelain for which once a fabulous price was paid has now become so cheap that it has nearly driven out earthen ware. In porcelain the base is fused and the glaze enters the substance; hence the ware is translucent. Earthen ware has not a fused base, but is porous inside. The glaze is put on the outside and does not enter the base; hence it peels off; hence too the ware is opaque. The chief materialof porcelain is kaolin, which is formed by the decomposition of felspar. The kaolin must be white, free from ferric oxide, which would give a brown color. But if kaolin alone were used the ware would shrink too much in baking; therefore a proportion of finely crushed sand and felspar or some fusible material is added. These materials are ground as fine as possible, mixed with water, kneaded, allowed to stand,

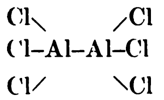
and kneaded again. The mixture is allowed to stand three months. During this time organic matter, if any is present, decomposes and gases are given off. This must be done to prevent the formation of bubbles in the heating. A single hair or a speck of dirt is enough to spoil a piece. When the material is free from all impurities, the articles are shaped. There are four ways in which this can be done. (1) By the potter's wheel. This is a horizontally revolving wheel, upon which the article is shaped with the hands or some rough tool. (2) By turning. One side of the article is shaped by placing the article on a plaster of Paris mould, set on a horizontally revolving stand. A profile of the desired shape is pressed on the upper surface, and by revolving the stand the shape is given. (3) By moulding. In this method the porcelain clay is rolled into sheets and pressed upon the mould with the hands or with a sponge. (4) By casting. The material is mixed to the consistency of thick cream and poured into a plaster of Paris mould. A little of it hardens and the rest is poured out. The process is repeated until a sufficient thickness is produced. The finest designs are made by sculpture. After shaping, the article is thoroughly dried and put into the furnace. The furnace has three stories and the heat enters the two lower through holes in the sides. Wood is constantly thrown in and, except in the Bessemer process, the highest heat obtained in the arts is secured. The draft is so powerful that it sucks ashes and all up chimney. The ware is first put in the upper chamber, where it is not thoroughly fused and hence is not very translucent. The ware in this stage is called *biscuit ware* and with an inside glazing is ready for use. To become porcelain it must be glazed on the outside and thoroughly fused. The glaze consists of ground felspar and sand suspended in water. The piece is dipped for a moment into this mixture, the base absorbs the water and the powder remains evenly spread over the surface. A little of the powder is also absorbed into the base itself. Before baking, the glaze is scraped off the bottom of the vessel to avoid fusion with the "seggars." These are boxes of porous infusible clay, in which the ware is put to keep off the ashes of the fire. The seggars are packed closely in the lower chambers of the furnace and the fire circulates about them. The glaze fuses and enters the pores of the base, which also fuses; so that there is no distinct dividing line between the base and the glaze, and the ware becomes translucent. Not until after several days, when the furnace has thoroughly cooled, is the finished ware removed. The chief causes of the high cost of porcelain are these: the great care needed to get materials free from impurities; the expense of firing the furnace; the fact that much of the ware shrinks unevenly, becomes distorted, and has to be thrown away. *Coloring under the glaze.* The biscuit ware readily absorbs any solution placed upon it, and hence this is the period chosen for decorating. The coloring matter, which consists of metallic oxides, is applied with a brush in the case of the more delicate pieces of work, and in other cases printed on the ware. In printing, the design is traced with the oxides on oiled paper, pressed on the ware, and absorbed into the pores. The pottery is then dipped in the glaze and fused. The colors of the oxides do not come out distinctly until after the fusing. Cobaltous oxide gives blue, chromic oxide green, ferric oxide brown, manganic oxide purple. Only a few colors can stand the heat of the second firing; hence much of the decorating has to be done *over the glaze.* The paints used in this method are obtained by grinding up glass colored by the metallic oxides and mixing it with oil. This paint, like gilding, is applied to the ware with a hair pencil. For gilding, powdered gold is used. The ware is heated in a muffle by a moderate heat, sufficient merely to fuse the colored glass and the gold. The gold comes out dull and has to be polished. The decoration over the glaze is rougher than that under the glaze, and is more liable to crack off. There are two other classes of pottery resembling porcelain in having a fused base. *Wedgewood ware* was invented in England at the beginning of the present century. It is usually a pale blue or sage green with white figures, but with no relief. It is opaque and not porous; sometimes glazed and sometimes unglazed. The finest variety of Wedgewood ware is cameo, which will stand examination with the microscope. Another form of ware with a fused base is *stoneware*, made of common clay with some iron in it. The base is fused and the ware is also glazed. The glaze is a salt glaze. Moist salt is thrown into the furnace, and, being volatilized, acts on the silicate of iron in the clay.

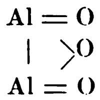
$$Fe_2(SiO_3)_3 + 6\ NaCl = 3Na_2SiO_3 + Fe_2Cl_6 .$$

The ferric chloride passes off in vapor and the sodic silicate, a sort of glass, remains as glaze. This stoneware is used for filter jars, jugs, and for any rough use. WARE WITH A POROUS BASE. *Earthen ware:* Majolica and Palissy ware come under this head. The base is not fused, and hence has to be glazed. It is sometimes hard to distinguish between Wedgewood ware (fused base) and earthen ware. Both are opaque, but when broken, porous earthen ware adheres to the tongue, while ware with fused base does not. In earthen ware the glaze is distinct from the base and of different composition. It does not enter the base and hence is apt to peel off. The glaze is a lead glass, and with a white base is transparent, but with a colored base it is made white, usually by stannic oxide, becoming a sort of enamel. The glaze is occasionally attacked by vinegar, and cases of poisoning from this cause have been known. The commonest form of earthen ware is English stone ware, made about like porcelain but not heated so high. Earthen ware varies in quality from this and even better ware, to bricks. Faience, named from the Italian city Faenza, is now synonymous with earthen ware. Doulton is also used in the same sense in England. Clay pipes are made of pure white clay. Flower-pots and bricks are made of clay colored by iron. Common bricks are dried in the sun and baked; firebrick is made of very infusible clay and stands heat better. Crucibles too are made of very infusible clay mixed with the powder of old crucibles to prevent shrinkage. The first factory in U. S. for artistic pottery was established about 1865 at Beverly. Soon after, others were started at Arlington and Chelsea. The one at Chelsea now makes an artistic greenish ware.

ALUMINIC OXIDE, Al_2O_3. The simplest formula for the chloride would be $AlCl_3$, regarding Al as trivalent; but as it is volatile its molec. wt. can be found, and this corresponds to the formula

Al_2Cl_6. The same fact holds good of every known compound of Al, *i. e.* the atom of Al never occurs single. Al then is regarded as quadrivalent, and the graphic symbols of Al_2Cl_6 and Al_2O_3 would be:





Al_2O_3 is the mineral corundum of which the sapphire is a transparent variety, and emery, a coarse impure variety with iron in it. Sapphires can be made artificially. Sapphire is inferior only to the diamond in hardness. Emery also is very hard, and is found in Naxos in boulders. In 1864 a vein of emery was discovered at Chester, Mass., and was at first thought to be an ore of iron. The emery from its hardness was so difficult to extract that the mine was at one time abandoned, but it is now worked. Emery powder is suspended in water; the coarse emery settles, the water is poured off, allowed to stand, a finer emery deposited, and the water again poured off. Thus we get emery of different degrees of fineness.

Aluminic Hydrate, $Al_2O_6H_6$, is prepared by action of NH_4OH on a soluble Al salt.

$$Al_2Cl_6 + 6NH_4OH = Al_2O_6H_6 + 6NH_4Cl.$$

It is insoluble and consequently has no reaction with test paper. It is of a gelatinous consistency, nearly transparent, and sometimes has to be boiled to become visible. It has peculiar properties; if we add NaOH to Al_2Cl_6, the hydrate is precipitated.

$$Al_2Cl_6 + 6NaOH = Al_2O_6H_6 + 6NaCl.$$

Upon adding an excess of NaOH, this precipitate redissolves, forming sodic aluminate.

$$Al_2O_6H_6 + 6NaOH = Na_6O_6Al_2 + 6H_2O.$$

In this case the $Al_2O_6H_6$ acts as an acid, allowing its H to be replaced by the basic radical Na. HCl dissolves it, forming Al_2Cl_6.

$$Al_2O_6H_6 + 6HCl = Al_2Cl_6 + 6H_2O.$$

Here the hydrate acts as a base, and with a strong base it acts as an acid; in fact it is on the border line between a base and an acid.

SODIC ALUMINATE, $Na_6O_6Al_2$, is soluble, white, and is used as a mordant to fix the colors in dyeing.

ALUMINUM, Al_2. Extraction: Al and an impurity, iron, exist in the ore as hydrates. The acid property of $Al_2O_6H_6$ is made the means of freeing it from the iron. It is heated with Na_2CO_3. At a high temperature $Al_2O_6H_6$ is a stronger acid than H_2CO_3, and hence the Na_2CO_3 will be broken up.

$$Al_2O_4H_2Fe_2O_4H_2 + 3Na_2CO_3 = Na_6O_6Al_2 + 3CO_2 + 2H_2O + Fe_2O_3.$$

The $Na_6O_6Al_2$ formed, being soluble, can be removed from the insoluble ferric oxide. The solution is treated with CO_2, and since at ordinary temperature carbonic acid is a stronger acid than $Al_2O_6H_6$, the sodic aluminate will be broken up.

$$Na_6O_6Al_2 + 3CO_2 + 3H_2O = Al_2O_6H_6 + 3Na_2CO_3.$$

These reactions illustrate Berthollet's law; in the first a volatile, and in the second, an insoluble substance is formed, and hence the reaction will be complete. The pure hydrate is heated.

$$Al_2O_6H_6 = Al_2O_3 + 3H_2O.$$

The oxide is now heated with C, Cl, and NaCl, forming a double chloride of Na and Al.

$$Al_2O_3 + 3C + 3Cl_2 + 2NaCl = Al_2Na_2Cl_8 + 3CO.$$

This is called a *concurrent reaction*. These reactions were first pointed out by Oersted. Neither the C nor the Cl has power alone to break up the Al_2O_3; but when the C works on the O, and the Cl on the Al, the oxide is easily pulled apart. The double salt is heated in a reverberatory furnace with Na.

$$Al_2Cl_62NaCl + 3Na_2 = 2Al + 8NaCl.$$

Properties: the metal, Al_2, is white, has a brilliant lustre, is but little tarnished by air, is as tough as copper and is very light; sp. gr. 2.56. Perhaps in the future it will supersede iron in many of its uses, especially for cooking utensils and ships. At present the method of extraction is too expensive. It fuses at 700° and does not burn easily; it is dissolved by NaOH, forming sodic aluminate.

$$Al_2 + 6NaOH = Al_2O_6Na_6 + 3H_2.$$

It is also slightly affected by NaCl. It is very sonorous when struck, too much so for bells, is malleable, and can be rolled into thin foil and drawn into fine wire. *Uses:* Al_2 is sometimes used on account of its lightness for mounting optical instruments, opera glasses, theodolites, etc.; for small weights and balance-beams in laboratories, and for jewelry. With copper it forms an alloy called aluminum bronze, which looks like gold, is not tarnished by air, and takes a high polish.

ALUMINIC CHLORIDE, Al_2Cl_6, may be obtained by action of HCl on the hydrate. [See reaction under $Al_2O_6H_6$.] If we try to get the anhydrous Al_2Cl_6 by evaporation, it is decomposed by the heat, HCl is driven off and $Al_2O_6H_6$ remains. Al_2Cl_6 may be prepared by Oersted's reaction above, leaving out the NaCl. It is very volatile so that its molec. wt. can be determined.

CRYOLITE, $Al_2F_{12}Na_6$, Sodic-Fluo-Aluminate, is found in Greenland and is called cryolite from its resemblance to ice. It is like $Al_2O_6Na_6$, except that each atom of O is replaced by two of fluorine, as if it were formed from the acid $H_6F_{12}Al_2$. It is used as a source of alum, of Na_2CO_3, and of hydro-fluoric acid.

ALUM, $K_2Al_2(SO_4)_4 24H_2O$ is used as a mordant in *Calico Printing*. If we boil cloth in a dye solution, some of the dye enters the cloth, but is easily washed out; hence a substance must be found that will adhere both to the dye and to the cloth. Such a substance is found in $Al_2O_6H_6$, which is precipitated from the mordant into the fibre of the cloth.. Any substance may be used as a mordant, from which a precipitate that will unite with the dye can be formed. The precipitate when united with the coloring matter forms a lake. In calico printing the mordant is applied by copper rollers engraved with the design. Different colors can be got by using rollers fed with different mordants — a separate roller for each. The calico has then to undergo the process called dunging. This consists in adding some alkaline reagent such as NH_4OH, Na_2CO_3, Na_2SiO_3 or Na_2HPO_4 to the mordant. Since the mordant used is usually some salt of Al, $Al_2O_6H_6$ or some basic aluminum salt is precipitated. The calico is boiled with the dye, and the dye unites with the precipitate to form the lake The color is fast, because the precipitate of course is insoluble in water and becomes entangled in the fibre of the cloth. The process of dunging received its name because the substance originally added to the mordant was cow-dung. This contains NH_4OH, and precipitates $Al_2O_6H_6$ in the cloth. If a ferric or stannic salt is used as a mordant, the color of the dye is modified by the color of the mordant. But with a pure aluminic salt the color is unchanged. The salts chiefly used are crystallized alum, sodic aluminate, or aluminic sulphate, called concentrated alum. A mordant is not necessary for all dyes. The process above described has been replaced by the process of *ageing and steam printing*, since in the latter case the design can be printed on the cloth with dyes of different colors at the same time. The cloth is printed with the dye mixed with aluminic acetate, the so called red liquor. This is prepared from alum and plumbic acetate.

$$Al_2(SO_4)_3 + 3Pb(C_2H_3O_2)_2 = 3PbSO_4 + Al_2(C_2H_3O_2)_6.$$

After printing, the cloth is hung up exposed to the air. The red liquor decomposes, leaving $Al_2O_6H_6$ precipitated in the cloth, making the color fast.

$$Al_2(C_2H_3O_2)_6 + 6H_2O = Al_2O_6H_6 + 6HC_2H_3O_2.$$

This exposure to air is called ageing. The decomposition of the red liquor is hastened by placing the cloth in a chamber filled with steam, — the process known as steam printing. *Preparation of Alum.* Roman alum is a pure alum obtained by calcining alumite, a basic aluminic sulphate associated with potassic sulphate. When calcined the substance becomes soluble in water, provided the heat be not too great, and alum can be dissolved out. This alum crystallizes, unlike other alum, in cubes. There are two methods of obtaining pure Al compounds: (1) by converting the salt of Al into sodic aluminate; (2) by the formation of alum. In (2), $Al_2(SO_4)_3$ is first made by dissolving some Al salt in H_2SO_4. This is converted to alum by adding the proper amount of H_2O and K_2SO_4. Alum instead of $Al_2(SO_4)_3$ is used to obtain pure Al salts, since it crystallizes better and hence can be more easily purified. This is the first of an important class of double sulphates or alums, all crystallizing in the same form with $24H_2O$, consisting of aluminic, ferric, chromic or manganic sulphates united with the sulphate of one of the alkaline metals, K, Na, NH_4, Rb, or Cs; *e.g.* $(NH_4)_2Cr_2(SO_4)_4 24H_2O$ an ammonio-chromic alum. Another method of making alum is by dissolving bauxite, clay, or slate in H_2SO_4. Aluminic sulphate mixed with ferrous sulphate is obtained. When K_2SO_4 or KCl is added, alum is formed.

$$Al_2(SO_4)_3 + FeSO_4 + K_2SO_4 = \text{alum} + FeSO_4 .$$
$$Al_2(SO_4)_3 + FeSO_4 + 2KCl = \text{alum} + FeCl_2 .$$

As the ferrous sulphate has a tendency to pass over to the ferric, the solution must be boiled with iron before the K salt is added. This reduces the ferric to the ferrous sulphate.

$$Fe_2(SO_4)_3 + Fe = 3FeSO_4 .$$

If this were not done we should obtain, when the K_2SO_4 is added, an alum having some iron in place of Al. The alum formed is crystallized out from the $FeSO_4$. During crystallization it is constantly stirred so that alum meal is formed. This is washed to get rid of the mother liquor. The meal is put into hogsheads and just enough hot water added to dissolve it. On cooling, the alum crystallizes out in large crystals. *Properties:* alum is white, has an acid reaction, is more soluble in hot than in cold water, and crystallizes in octahedra with the angles cut off. *Uses:* used as a mordant and to adulterate bread; added to poor flour it makes a better looking but unwholesome bread.

ULTRAMARINE was formerly obtained from lapis lazuli, and was almost as expensive as gold. Now it is made from Kaolin, Na_2CO_3, C, and S heated. The peculiarity of it is that all these substances give white or colorless compounds, but when combined, give this brilliant blue. Its exact constitution is unknown, but it contains Al, O, Si, Na, and S. It is used as a pigment, not as a dye, and is now very cheap.

Classification of the Elements. All attempts to classify the elements were unsatisfactory until in 1873, Mendelejeff, a Russian chemist, published his method. Very much the same method was worked out by Meyer, a German chemist, in the same year, but Mendelejeff's classification is better and more complete. It is arranged on the principle that the properties of the elements are periodic functions of their atomic weight, *i.e.*, that their properties vary regularly and periodically with the increase in the at. wts. We begin the classification with H, whose at. wt. is 1, and leave the rest of the first row for the present. The element next to H in at. wt. is Li, 7, which we place under H; next in this second row we place glucinum G, 9.4, then boron B, 11, and so on. Li has strong basic properties, but the basic properties decrease as we go along the row to the right, while the acid properties increase. From fluorine (F), which forms the very strong hydrofluoric acid (HF), to Na the element next in at. wt., which forms strong basic compounds, there is a jump in the properties; therefore we put Na under Li at the beginning of a new row. This third row again goes from elements that form strongly basic, to those that form strongly acid compounds. On the dividing line between bases and acids we sometimes find an element which acts both as a base and as an acid; in the third row for example, Al, the hydrate of which it will be remembered can be both a weak base and a weak acid. Basic properties become more marked as we go down the series: thus rubidium and caesium are much stronger bases than potassium. The elements of the first series form the oxides H_2O, Li_2O, etc., which can be represented by the general formula R_2O. The second series form oxides MgO, CaO, etc., which can be represented by RO, or, to make it symmetrical with the formulas of the other series, R_2O_2. The third series form oxides such as B_2O_3, Al_2O_3 represented by R_2O_3. The fourth series, SiO_2, represented by R_2O_4; fifth series, N_2O_5, or in general R_2O_5; sixth series SO_3, or R_2O_6; seventh series Mn_2O_7, or R_2O_7. Thus from each series to the next, the amount of O which combines with two atoms of the element increases by one atom. The first series forms hydrates NaOH, KOH, etc., represented by HOR; the second series, MgO_2H_2, or H_2O_2R; third series, $Al_2O_6H_6$, or H_3O_3R; the fourth series, H_4SiO_4, or H_4O_4R; the fifth series H_3PO_4, or H_3O_4R (which may be regarded as $H_5O_5R - H_2O$); the sixth series, H_2SO_4, or H_2O_4R ($H_6O_6R - 2H_2O$); the seventh series, $HClO_4$ or HO_4R ($H_7O_7R - 3H_2O$). It must be borne in mind in considering the above that a hydrate is either a base or an acid, according as the radical which enters into it is a basic or acid radical. The elements of the first three series form no hydrides, but in the fourth series the hydrides begin, *e.g.*, CH_4 represented by RH_4. In the fifth series we have NH_3 or RH_3, in the sixth H_2O or RH_2, in the seventh HCl or RH.

CLASSIFICATION.

The properties of the elements are periodic functions of their atomic weights.

MENDELEJEFFS TABLE.

	R_2O. HOR.	R_2O_2. H_2O_2R.	R_2O_3. H_3O_3R.	R_2O_4. H_4O_4R. RH_4.	R_2O_5. H_3RO_4. RH_3.	R_2O_6. H_2RO_4. RH_2.	R_2O_7. HRO_4. RH.	R_2O_8.
1	H 1.							
2	Li 7.	G 9.4?	B 11.	C 12.	N 14.	O 16.	F 19.	
3	Na 23.	Mg 24.	Al 27	Si 28.	P 31.	S 32.	Cl 35.5.	
4	K 39.1.	Ca 40.		Ti 48.	V 51.	Cr 52.2.	Mn 55.	Fe 56. Co 59. Ni 59.
5	Cu 63.4	Zn 65.2.			As 75.	Se 78.	Br 80.	
6	Rb 85.	Sr 87.	(Yt 88.)	Zr 90.	Nb 94.	Mo 96.		Ru 104. Rh 104. Pd 106.
7	Ag 108.	Cd 112.	(In 113.)	Sn 118.	Sb 120.	Te 125?	I 127.	
8	Cs 133.	Ba 137.	(La 139.)	(Ce 140.)				
9								
10			(Er 178.)		Ta 182.	W 184.		Os 195. Ir 197. Pt 197.4.
11	Au 199.	Hg 200.	Tl 204.	Pb 207.	Bi 208.			
12				Th 231.		(U 240.)		

In the fourth row we have K 39.1, Ca 40, and next Titanium, Ti, 48. Here occurs a wide jump from 40 to 48. Moreover Ti forms two oxides, Ti_2O_3 and TiO_2. If we take the highest oxide as the typical oxide, Ti will come under Si and a place will be left vacant under Al. Ti is more like Si and Zr than it is like Al and B, so we conclude that it belongs where we have placed it and that some element is wanting or has not been discovered.

From its at. wt. Fe should begin the fifth row, but it is both bivalent and quadrivalent and we have the oxides FeO_3, Fe_2O_3, and FeO. The oxide of the first series is R_2O; hence we cannot put iron into the system. In the same way neither Co 59 nor Ni 59 will fit in, so we place them outside the table in an eighth series. In the fifth row we have Cu 63.4, Zn 65.2 and then a jump to As 75. As forms an oxide As_2O_5 which would correspond to the oxides of the fifth series; for these reasons we place it in the fifth series, leaving vacancies in the third and fourth. In the sixth row Ruthenium, Ru, 104 comes next after Molybdenum, Mo, 96; but it cannot be placed in the seventh series, since it forms an oxide RuO_4. From their at. wts. and the oxides which they form, neither Rhodium, Rh, nor Palladium, Pd, can be fitted into the system and so we place them with Ru in the eighth series. Te 128 will not fit into the seventh row, and Os, Ir, and Pt will fit neither in the tenth row nor in the eleventh. In at. wts. these last three lie between the two rows, and Os forms an oxide OsO_4, like RuO_4. Therefore we place them in the eighth series.

We have left out of the table the nine elements which we have put together arbitrarily in an eighth series, and the elements Yttrium, Didymium, Tellurium, Lanthanum, Cerium, Erbium, Uranium and Indium. Although Os does not fit even into the eighth series with the at. wt. usually given it, 199.1, we shall see later that it really does belong there. H is put in the first row, first series, since it forms the oxide H_2O; all the rest of the row are wanting. All the nine elements of the eighth series stand at the end of even rows and therefore are arranged symmetrically. We have reason to consider them a true series with three in a row instead of one. If we are correct in this, the elements ought to resemble each other. This they do; they are all nearly infusible, white,

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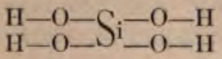
hard metals. All the strongly magnetic elements belong to this series. The only metals that absorb H are in the eighth series. This property is called occlusion, is possessed by Ni and Pd and to a less exent by Fe. Another reason for placing them in this series is that Ru and Os give oxides of the general form R_2O_8. But there is a still better argument. We find between Cl and K as marked a difference as possible, Cl being acid and K being basic: but between Mn and Cu the difference is not very great. Both give basic compounds and both are metals. So in general between the end of the odd rows and the beginning of the even, the difference is great, while between the end of the even and the beginning of the odd, the difference is not very great. The eighth series forms the connecting link in properties, between the end of the even, and the beginning of the odd rows. Iron and the two elements under it, Ru and Os, form cyanides with the alkaline metals, *e. g.* $K_4Fe(CN)_6$ potassic ferro-cyanide, $K_4Ru(CN)_6$ (ruthenio-) and $K_4Os(CN)_6$ (osmio-). Cobalt and the elements under it, Rh and Ir, also form cyanides, as $K_6Co_2(CN)_{12}$ potassic cobalticyanide, $K_6Rh_2(CN)_{12}$ (rhodi-), and $K_6Ir_2(CN)_{12}$ (iridi-). Nickel and the elements under it, Pd and Pt, form double cyanides with the alkaline metals, as $2KCNNi(CN)_2$ or $K_2Ni(CN)_4$, $K_2Pd(CN)_4$, and $K_2Pt(CN)_4$. It must be understood that each of these three last is a double cyanide of two elements, while the others are potassic salts of cyanic acids, *e. g.* $K_4Fe(CN)_6$ formed from hydro ferro-cyanic acid, $H_4Fe(CN)_6$.

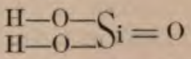
Since the eighth series forms this connecting link between the even and odd rows, we can remove the fifth row bodily and add it to the fourth row, so that Cu will come next to Ni. In the same way we can transfer the seventh to the end of the sixth, and the eleventh to the end of the tenth. Also we can place the third row after the second, provided we leave three blank spaces between F and Na, so that Na comes over Cu. These are called Mendelejeff's *great periods.* By this means we bring the elements into such a position that all those in a series are very much alike. In the *small periods* the greatest resemblances occur between those standing alternately in a series, and not those that stand next each other. The resemblances however, do not get fairly started until we reach about the fourth row in the small periods. This is illustrated by the analogy of organic chemistry. In organic chemistry radicals are treated like elements, and they can be grouped in series like elements.

CH_3	C_2H_3	(HOH)
C_2H_5	C_3H_5	CH_3OH
C_3H_7	C_4H_7	C_2H_5OH
C_4H_9	C_5H_9	C_3H_7OH
		C_4H_9OH

The two left hand columns are the first members of two series of hydrocarbons, and the right hand column is the beginning of the group of alcohols, hydrates of the first series. Regarding each member of the group of alcohols as formed from the one below it by subtracting CH_2, we arrive at CH_3OH (wood-alcohol) and HOH (water), which have very little resemblance to the lower members of the group. The fact that there is little resemblance in characteristic properties between the first element in a series and those that follow it, is brought out by the hydrates. In the fourth series the normal hydrate is H_4RO_4. Si has this hydrate, C has not; but Si also has a hydrate H_2SiO_3, like H_2CO_3, which may be regarded as the normal hydrate minus H_2O.



$$\begin{array}{l}H—O—\\H—O—\end{array}Si\begin{array}{l}—O—H\\—O—H\end{array}$$



$$\begin{array}{l}H—O—\\H—O—\end{array}Si = O$$

In the fifth series the normal hydrate is H_3RO_4. P has this hydrate, H_3PO_4, and also HPO_3, corresponding to HNO_3, which may be regarded as the normal hydrate minus H_2O. There is no hydrate of oxygen. If we suppose one, H_2OO_3, like H_2SO_3, and subtract H_2O as before, we have left O_3 or ozone. F in the seventh series differs from the other elements in the series, and in fact from all other known elements, in that it does not combine with oxygen.

This system of classification is not an arbitrary one. If an element should be discovered with the at. wt. 50 and an oxide R_2O_5, we could not fit it into the system, as the place is already occupied by vanadium. Such a discovery would overthrow the whole classification. The elements Te, Yt, Di, La, Ce, Er, U, and In, as has been said, do not fit into the system with the at.

wts. hitherto assigned them. Therefore if the classification be correct, their at. wts. must have been wrongly determined, either because the analyses were badly done or because not enough was known about their compounds. Mendelejeff thought that a mistake had been made in the analysis of Te and that the at. wt. should be 125 instead of 128; therefore he put Te into the sixth series after Sb, with that at. wt. Likewise he supposed the analyses of Au and Os to be wrong. Mendelejeff is very probably right in regard to Os, since it is very rare, and also in regard to Au, since its attraction for other elements is very weak. His proposed change was, in the case of Os, from an at. wt. of 199.1 to 195, and in the case of Au, from 197 to 199. Mendelejeff did not discredit the analyses of the other elements, but he supposed that wrong formulas of their compounds were taken as the basis for determining the at. wt. One method of determining atomic weights is by studying the relations of elements and reasoning by analogy. In this way we suppose that the formula of the oxide of an element is the same as that of some other element which it resembles. The compounds of In resemble those of Zn, and it is supposed by analogy that the formulas of the compounds of In resemble those of the compounds of Zn. We know by experiment that the oxide of In has 76 parts of In to 16 of O. If, therefore, the formula of the oxide is InO, like ZnO, the at. wt. of In would be 76. But with this at. wt. In does not fit into the table; consequently Mendelejeff tried to change the formula of the oxide, and supposed it to be In_2O. In this molecule the weight of oxygen being 16, the weight of indium must be 76, since they combine in the proportion of 76 to 16. The wt. of two atoms of In therefore being 76, the wt. of one atom would be one half of 76, or 38. But with this at. wt. again In would not fit. So being unable to put it into either the first or second series, Mendelejeff tried the oxide of the third series, or In_2O_3. Here the wt. of O being 48 or 3×16, the wt. of In must be 3×76, or 228. One atom of In therefore would be 114. (The latest result of analysis is 113.) With this oxide and this at. wt. In fits into the third series, seventh row. That this is the correct place requires further proof. This is found by determining theoretically the properties of the element which should occupy this place and comparing them with the observed properties of In. The sp. gr. should lie between those of Cd and In, *i. e.* should be about 7.9; also Al and Tl are symmetrical to this place and the mean of their sp. grs. is about 7.2. By experiment the sp. gr. of In is found to be 7.4, or nearly half way between the calculated results. In should give a gelatinous oxide like Al, and so it does. Its sulphide should be insoluble in acids, and so it is. Thus there can be no doubt that In should stand where it does, and this result has been generally accepted. The other unclassified elements forming the cerium group give more trouble; they are closely related and their properties are similar but they are very rare. They were fitted in theoretically by Mendelejeff. Recently one or two of them have been found in considerable quantities by Hillebrand, an American chemist, the specific heats determined, the atomic weights verified, and the position assigned by Mendelejeff justified for Ce and La. The discovery of the element gallium in 1876 tended greatly to confirm Mendelejeff's classification. When he first heard the properties of Ga, he predicted that it was *ekaaluminum*, *i e.* next to aluminum, and said that its at. wt. should be very near 68. It has since been determined experimentally to be 69.2; and in fact all the observed properties of Ga correspond to those of ekaaluminum.

Résumé. Taking the second series as a typical series, the elements that stand next but one to each other are closely related, and the difference in qualities is only such as would be caused by increase of atomic weight. The water of crystallization diminishes as we go down; mercuric sulphate has none. Taking the third row as a typical row, the properties vary perceptibly as we go along. NaOH is strongly alkaline, soluble, and Na cannot be exposed to air; MgO_2H_2 is alkaline and slightly soluble, the metal Mg is permanent and burns in the air; $Al_2O_6H_6$ is insoluble, both an acid and a base, and the metal Al_2 will not burn in air; H_4SiO_4 is an acid, and in silicon the metallic properties disappear; the phosphoric acids are strong acids and phosphorus is a non-metal; sulphur is a non-metal, H_2SO_4 is a strong acid, and the hydride H_2S is a weak acid: chlorine is a non-metal and the hydride HCl is a strong acid. Among the weak points in

Mendelejeff's classification are these. Mercury is closely related to copper and yet stands far from it. Lead is closely related to barium, but is not near it in the table. Glucinum whose at. wt. was formerly thought to be 9.4, with an oxide GO, fitted into the 2nd row next to Li. But the oxide has since been shown probably to be G_2O_3, and the at. wt. to be about 14. Consequently G cannot now be placed in the table. Similarly the at. wt. of didymium, which was thought to be 138, has now been found to be 145. Therefore Di must also be left out of the table.

Chromium, Cr, at. wt. 52.2, was discovered in 1797 by Vauquelin. The most important source of Cr is *chrome iron*, $FeCr_2O_4$. It is not rare and is found near Baltimore. We may look upon it either as a real compound of Cr — a ferrous salt derived from $H_2Cr_2O_4$ by replacing the H_2 by Fe, or as a double oxide $FeOCr_2O_3$. Chromium has three classes of salts, the chromous as CrO, $CrCl_2$, in which it is bivalent, the chromic as Cr_2O_3, Cr_2Cl_6, in which it is quadrivalent, and the chromates as CrO_3 in which it is sexivalent. Cr forms colored compounds. Nearly all the compounds of elements hitherto treated have been either white or colorless.

I. THE CHROMATES. POTASSIC CHROMATE, K_2CrO_4, is made by heating chrome iron in the air with calcic oxide and potassic carbonate. The CaO does not enter the reaction, but merely favors oxidation by keeping the mass porous.

$$FeOCr_2O_3 + 2K_2CO_3 + 3O = 2K_2CrO_4 + 2CO_2 + FeO.$$

The FeO at once passes to the ferric oxide, but for the sake of simplicity it is left out of the reaction above. The process is this:

$$2FeO + O = Fe_2O_3.$$

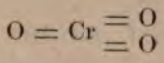
Since the chromate formed is soluble, it can be washed out from the insoluble ferric oxide and obtained by evaporation. Its color is yellow. When H_2SO_4 in excess is added to it, H_2CrO_4 is probably formed, but this at once breaks up into CrO_3 and H_2O.

$$K_2CrO_4 + H_2SO_4 = K_2SO_4 + H_2O + CrO_3.$$

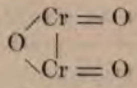
Consequently H_2CrO_4, which would be the normal hydrate corresponding to H_2SO_4, cannot be obtained. The salts of this acid resemble the corresponding sulphates, as we should expect since Cr is next below S in the sixth series of Mendelejeff's table.

Chromic Anhydride, CrO_3, is red, and soluble in water but not in strong H_2SO_4. Consequently in the above reaction it is precipitated. It cannot be obtained, however, by filtration, since it is a powerful oxidizer and would attack the filter paper. CrO_3 has very slight stability. If we put some dry CrO_3 into alcohol, it gives up part of its O to the alcohol, becoming Cr_2O_3 (green), and so much heat is evolved that the alcohol takes fire.

$$2CrO_3 = Cr_2O_3 + 3O \text{ (in combination with the alcohol).}$$



$$O = Cr \begin{matrix} = O \\ = O \end{matrix}$$



$$O \begin{matrix} \diagup Cr = O \\ \quad | \\ \diagdown Cr = O \end{matrix}$$

The quantivalence of Cr here changes from six to four. If to CrO_3 in solution in an acid, as HCl, boiling alcohol be added, the action is very violent and the liquid is turned from red to dark green.

$$2CrO_3 + 6HCl = Cr_2Cl_6 + 3O \text{ (in combination with the alcohol)} + 3H_2O.$$

With a substance more easily oxidized than alcohol, as H_2S, boiling is unnecessary. The color changes here as above with the quantivalence.

$$3H_2S + 2CrO_3 + 6HCl = Cr_2Cl_6 + 3S + 6H_2O.$$

The S falls in a white precipitate. In all these reactions the quantivalence of Cr changes from six to four. Whenever the quantivalence changes from a higher to a lower, there is always present some reducing agent.

Whenever the quantivalence changes from a lower to a higher there is present some oxidizer. Here the change is from four to six.

$$Cr_2O_3 + 2K_2O + 3O = 2K_2CrO_4.$$

These reactions involving changes of quantivalence form a fourth class of reactions to be added to those on p. 5.

Potassic Dichromate, $K_2Cr_2O_7$, is prepared by adding H_2SO_4 to K_2CrO_4. If the acid is in excess, we get the third reaction under potassic chromate. If it is not in excess, only a part of the K_2CrO_4 is converted to CrO_3, thus:

$$2K_2CrO_4 + H_2SO_4 = K_2SO_4 + K_2CrO_4CrO_3 + H_2O.$$

That is, the dichromate may be regarded as a compound of K_2CrO_4 and CrO_3. Its color is orange red, midway between the colors of its two components, CrO_3 and K_2CrO_4. It is an anhydro- or diacid salt. An *anhydro-* or *diacid* salt is a compound of the anhydride and a neutral salt. If to the dichromate we add an alkali, as KOH, it is changed back to the chromate.

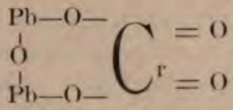
$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O.$$

$K_2Cr_2O_7$ is soluble and crystallizes easily. On this property depends its use as a source of the other Cr compounds, instead of K_2CrO_4, which crystallizes badly and is therefore hard to get pure. For this reason the dichromate is the most important of the Cr compounds. It is used in dyeing yellow. A very important use is its use as an oxidizer. Acids set free from it CrO_3 which readily gives up O. This quality is used in making a black dye. Potassic dichromate is also used in the *heliotype process* or photolithography. The principle of this is the action of sunlight on a mixture of gelatine and the dichromate. A photographic negative is taken, and in this, metallic silver corresponds to the light parts of the object or engraving to be copied, while transparent glass corresponds to the dark parts. A plate of gelatine usually with alum added to make it tougher is soaked in $K_2Cr_2O_7$. The negative is then placed over the gelatine in the sunlight, and wherever the glass is transparent the light strikes through and renders the gelatine plate insoluble and of a brown color. The plate is then taken to a dark room and the rest of the $K_2Cr_2O_7$ washed off. The plate is inked with a greasy ink which adheres only to the dry parts, *i.e.* insoluble $K_2Cr_2O_7$, corresponding to the dark parts of the object.

PLUMBIC CHROMATE, $PbCrO_4$, chrome yellow, can be made from $K_2Cr_2O_7$ or K_2CrO_4 by adding a soluble salt of lead. It is usually made by adding plumbic acetate, or sugar of lead to K_2CrO_4.

$$K_2CrO_4 + Pb(C_2H_3O_2)_2 = PbCrO_4 + 2KC_2H_3O_2.$$

It is one of the best of yellow paints and can be used also as a dye. When precipitated in the fibre of the cloth it gives to the cloth a yellow color which cannot be washed out. When combined with blue it gives a green color. On fusing, it becomes brown and is sometimes used in organic analysis. Since the substance to be analyzed must be burned in an enclosed space, O cannot be drawn from the air and therefore is supplied by $PbCrO_4$. The CO_2 and H_2O are collected in tubes and weighed, and thus the amount of H and C can be determined. *Chrome orange*, $PbOPbCrO_4$, is a basic plumbic chromate in which the oxide occurs instead of the hydrate.



Chrome red is a fuller red and is formed by adding to $PbOPbCrO_4$ still another PbO. Various chromates of other metals can be formed by adding K_2CrO_4 to a soluble salt of the metal, often the chloride. Baric chromate, $BaCrO_4$, is a pale yellow; mercurous chromate, Hg_2CrO_4, a brick red; ferric chromate $Fe_2(CrO_4)_3$, light red; and argentic chromate, Ag_2CrO_4, dark red.

Potassic Perchromate, blue, formula unknown, is a test for H_2O_2.

II. Chromic Compounds. In these compounds, corresponding to the oxide Cr_2O_3, Cr is quadrivalent.

Chrome Alum $K_2Cr_2(SO_4)_4 24H_2O$. Cr from its resemblance to Al would naturally be expected to form an alum. It is formed by adding H_2SO_4 to $K_2Cr_2O_7$. Oxalic acid or some other reducing agent must also be present to remove O from the dichromate.

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2C_2O_4 + Aq = K_2Cr_2(SO_4)_4 \\ 24H_2O + 7H_2O + 6CO_2 .$$

If this is allowed to evaporate spontaneously, purplish red crystals are formed so dark that they look black. If evaporated by heat, green or purplish black crystals are formed. If evaporated to dryness a green non-crystalline mass is the result. Chrome alum is used as a mordant. NH_4OH precipitates from it chromic hydrate, $Cr_2O_6H_6$. This clings to the cloth and takes up coloring matter, but its own color (greenish gray) mixes with the dye and modifies the lake. By carefully regulating the conditions, the hydrate can be got of a brilliant green. This is called Guignet's green, and forms a valuable pigment. $Cr_2O_6H_6$ is gelatinous like $Al_2O_6H_6$. When heated it gives up $3H_2O$ forming chromic oxide, Cr_2O_3, of a bright emerald green. It is often used for painting blinds, for coloring glass, and for coloring porcelain, where it can be used under the glaze. It is the Cr_2O_3 which gives to emerald its color.

CHROMIC CHLORIDE, Cr_2Cl_6, can be made according to the reaction under chromic anhydride and also by the following which is a concurrent reaction.

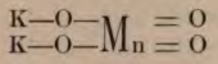
$$Cr_2O_3 + 3C + 3Cl_2 = Cr_2Cl_6 + 3CO.$$

This method of making Cr_2Cl_6 produces the red modification. The chloride distills over in violet scales. The reaction under CrO_3 produces the green modification. Cr_2Cl_6 when pure is red and insoluble, but the green modification is soluble. If, however, chromous chloride be added to the red modification + aq., it dissolves at once, forming the green modification. These green and red modifications occur in all the chromic compounds. The most probable theory in regard to them is that the green modification is a mixture of an acid and a basic salt, while the red modification is the normal salt.

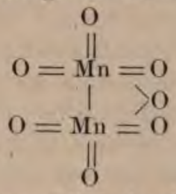
III. THE CHROMOUS COMPOUNDS are unimportant. In these Cr is bivalent. They must be kept from the air or else they pass into the chromic compounds. The color of the chromous compounds is blue or, when anhydrous, white.

Manganese, Mn, at. wt. 55. It was first recognized as a separate element in 1774 by Gahn. The chief interest in Mn, as in Cr, is chemical. Not more than seven or eight elements are more common than Mn. It is widely diffused and occurs in large quantities in certain places. It is found in nature chiefly as an oxide MnO_2, Pyrolusite, or as a hydrate $Mn_2O_4H_2$, Manganite. Of these, Pyrolusite called also Black Oxide of Mn is the more important. It is a very dirty substance, smutting the fingers. This property is characteristic of all minerals containing Mn. Wad, a mixture of several oxides of Mn, is found in many localities.

OXIDES OF MN. Mn forms several well defined oxides: *manganous* oxide, MnO, *manganoso-manganic* oxide, Mn_3O_4, *manganic* oxide or sesquioxide, Mn_2O_3, *manganic* dioxide, MnO_2, *permanganic* oxide or anhydride, Mn_2O_7. In the first, MnO, Mn is bivalent, in the next three it is quadrivalent, but in Mn_2O_7 it is octivalent. Mn forms salts corresponding to each of these oxides except Mn_3O_4. It also forms another series of salts called manganates, in which Mn is sexivalent. The oxide corresponding to these would be MnO_3, but it is unknown. The graphical formulas of the potassic manganate and of Mn_2O_7 are given below:



$$\begin{matrix} K-O- \\ K-O- \end{matrix} Mn \begin{matrix} =O \\ =O \end{matrix}$$



$$\begin{matrix} & O & & \\ & \| & & \\ O= & Mn & =O & \\ & | & & >O \\ O= & Mn & =O & \\ & \| & & \\ & O & & \end{matrix}$$

Black oxide of Mn, MnO_2, sometimes called the **Peroxide**, usually occurs in commerce as a black powder. Its most important use is in making chlorine.

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O$$
$$= MnCl_2 + Cl_2 + 2H_2O.$$

The manganic chloride, $MnCl_4$, formed in the first reaction, is very unstable and is broken up by slight heat, giving off free chlorine. This chlorine is then used for bleaching cotton cloth and linen. Another property of MnO_2 is its readiness to give up O, passing into a manganous compound.

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$

MnO_2 was formerly used as a source of O, but a better way of obtaining it is by heating $KClO_3$. [Explained under Chlorine.] If the $KClO_3$ is mixed with a little MnO_2, it parts with its O at a lower temperature. Upon the oxidizing qualities of MnO_2 depended its former use in decoloring glass. Glass was often colored green by an impurity, ferrous oxide FeO. Upon adding MnO_2 this was converted to ferric oxide, yellow or reddish brown.

$$2FeO + O \text{ (from } MnO_2) = Fe_2O_3.$$

Besides the Fe_2O_3, MnO, colorless, is formed. If therefore we add just enough MnO_2 to convert the ferrous to ferric oxide, we get a yellowish tinge in the glass. Upon adding a little more MnO_2, which is violet, the glass becomes colorless, since yellow and violet are complementary colors. From this property MnO_2 is called "glass maker's soap"; for the same reason it is also called Pyrolusite (πῦρ, λύω.) If glass decolored in this way be exposed to sunlight, it gradually changes to violet, probably owing to the oxidation of MnO to MnO_2. This method of decoloring glass is now no longer used, as it is easier to choose materials for the glass which are free from FeO, and thus violet glass in a house is a proof of its antiquity and is prized accordingly. MnO_2 is used in staining glass purple, called amethystine glass.

MANGANOUS SALTS. These are the most stable of the salts of Mn, while chromous salts are very unstable. On the other hand chromic compounds are the most stable salts of Cr, while the manganic salts are very unstable. *Manganous chloride*, $MnCl_2$, is one of the products in the reaction for making Cl from MnO_2. It is of no use and was formerly thrown away, but it is now reconverted to MnO_2 and used over again. It is soluble, and has a neutral reaction since Mn is a strong basic radical. It is of a rose pink color, which is characteristic of all soluble manganous salts. Insoluble manganous salts are white and generally unstable. *Manganous sulphate*, $MnSO_47H_2O$, is of a lighter color than $MnCl_2$. It can form double sulphates with potassium and ammonium, as $MnSO_4K_2SO_46H_2O$. This is a strong point of resemblance between Mg and Mn. *Manganous hydrate*, MnO_2H_2, is white, but on exposure to air it is converted to manganic hydrate (brown).

$$2MnO_2H_2 + O = Mn_2O_4H_2 + H_2O.$$

This turning brown of insoluble manganous salts is very characteristic. MnS is flesh-colored, and like the hydrate absorbs O from the air and becomes dark. It is soluble in acids, insoluble in alkalies. Mn_3O_4 is red; its constitution is unknown, but it might be looked upon as itself constituting a salt formed from $H_2Mn_2O_4$ by replacing H_2 by Mn. Mn can form an alum, as we should expect from its resemblance to Al. $K_2Mn_2(SO_4)_424H_2O$ is very unstable, being decomposed by water.

POTASSIC MANGANATE, K_2MnO_4, is made from MnO_2 by KOH.

$$2KOH + MnO_2 + O = K_2MnO_4 + H_2O.$$

The quantivalence of Mn changes here from a lower to a higher, and hence O is taken up. The color of the manganate is dark bluish green. It is so marked that it is used as a test for Mn, the Mn, if any is present, being converted to K_2MnO_4. The manganate is very unstable; upon the addition of an acid it changes color, owing to the formation of potassic permanganate (red). The same change takes place on boiling the manganate, and also more slowly in the air at ordinary temperatures. Owing to the fact that it changes color so readily it is sometimes called "chameleon mineral." Owing to this instability we cannot get H_2MnO_4.

Potassic Permanganate, $K_2Mn_2O_8$, is usually obtained from the manganate by boiling, or by addition of an acid. It is soluble, like all permanganates, forming a pinkish purple solution. It readily gives up O and hence cannot be freed from its impurities by filtration through paper, as it burns the paper. This property of giving up O leads to an important use in the analysis of iron ore. The ore is converted to ferrous sulphate, $FeSO_4$. This is dissolved in H_2O and a little H_2SO_4 is added. A standard solution of $K_2Mn_2O_8$ is made and poured into the solution of $FeSO_4$. The ferrous sulphate present is converted to the ferric.

$$2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O.$$

The permanganate is at the same time reduced and loses its purple color; but when all the ferrous sulphate has been changed to ferric, the next drop of $K_2Mn_2O_8$ distinctly colors the solution. The amount of $K_2Mn_2O_8$ used can be read off from a graduated scale, and the amount of Fe in the ore calculated [cf. soap test for hardness of water]. $K_2Mn_2O_8$ easily oxidizes alcohol or any organic substance, being reduced to one of the lower oxides. Therefore it is used as a disinfectant, burning up putrid flesh, as in diphtheria. If it is added to alcohol which has been previously heated, the O given off will set fire to the alcohol. If $K_2Mn_2O_8$ be mixed in a mortar with powdered sulphur, and the mixture be rubbed round quickly, it burns with a series of little snaps or explosions. This illustrates the great ease with which it gives up O. The permanganate is not reduced by acids, and therefore we can get permanganic acid, $H_2Mn_2O_8$. It is formed by adding an acid, as H_2SO_4, to $K_2Mn_2O_8$. It is a brownish liquid, very unstable. It volatilizes even in a sealed tube, forming a pink vapor, which gives the true color of the acid. The permanganate is converted to the manganate by adding an alkali.

$$K_2Mn_2O_8 + 2KOH = 2K_2MnO_4 + H_2O + O.$$

This reaction takes place if there is present a reducer, as alcohol, to take up the O.

Iron, Fe, at. wt. 56, is one of the commonest of the elements. The earth's crust is composed chiefly of the following elements in the order of abundance: O, Si, Al, Ca, Fe, Mg, K, Na. The dark brownish color of earths and rocks is almost always due to Fe. Iron, however, is extracted only from rocks or substances that contain much of it. Those substances from which metals are usually obtained are called *ores* of the metals. ORES. The richest of the ores of Fe is *Magnetite*, $FeFe_2O_4$. It is almost black, usually granular, and makes a black streak on unglazed porcelain. It is magnetic and some varieties are natural magnets called lodestones. The ore next in richness is *Haematite* (αιμα), Fe_2O_3, a shiny mineral sometimes crystalline. It usually occurs so compact that it looks black, but all varieties give a red streak on unglazed porcelain. Red chalk and Red ochre are earthy varieties of haematite. *Limonite*, an abnormal hydrate, varies in color from yellow, which is a loose variety, to black, which is more compact. It makes a yellow mark on unglazed porcelain, and is used as a pigment under the name of yellow ochre. It never occurs crystallized. Bog ore is an impure limonite deposited from iron temporarily hard water. [See under $FeCO_3$]. *Siderite*, $FeCO_3$, is one of the ores poorest in iron, but at the same time one of the most valuable. It resembles calcite, and, when it has not been exposed to the air, is nearly as white; in air however it turns brown, and it gives a brown streak on unglazed porcelain. Clay ironstone is an impure siderite containing very little iron, but it is one of the most important ores. It is from this ore that nearly all British iron is made. Magnetite makes the best iron; Russian and Norway iron are made from magnetite. The value of an iron ore depends not so much upon its richness, as upon its proximity to beds of coal and limestone, which are necessary for its reduction. Iron Mountain is nearly pure magnetite, but has never been worked till recently, because of its distance from coal and limestone. The nearness of coal and limestone is what gives the English clay ironstone its value. NOT ORES. *Iron Pyrites*, FeS_2, is of the color of brass and is called "fool's gold." It is almost worthless as an ore of Fe, because the separation of S from it is so expensive. Of late years it has been used as a source of S in the manufacture of H_2SO_4. After this process, it is left in a condition to be used as an ore of Fe; but the Fe obtained in this way is not very good, owing to the impossibility of removing the last traces of S. *Mispickel*, $Fe[S_2As_2]$ is used as a source of As. Iron occurs native in *Meteorites*, usually alloyed with nickel; but seldom, if ever, of terrestrial origin.

EXTRACTION. *Cast iron. Blast Furnace.* Cast iron is a compound of Fe and C; it is brittle and fuses at 1300°; wrought iron is nearly pure iron, and is tougher and less fusible than cast iron. The form of the blast furnace is that of two truncated hollow cones, placed base to base. The hollow interior of the cones is termed the *shaft*, and the wide part below the junction of the cones is known as the *boshes*. The bottom of the shaft terminates in the *hearth*, the sides of which are sometimes vertical but are now usually made sloping. The bottom of the hearth is called the *crucible*. In the blast furnace any ore may be used. The shaft is first wholly filled with coal, which burns and settles. Ore is next dumped in, then a flux, then coal, ore, flux, and so on in layers. The process is in theory the same as in the extraction of Zn, *i. e.* to convert the ore to the oxide, and then remove O by C and get the metal. But as iron is not volatile it cannot, like Zn, be removed from the gangue by distillation; therefore a flux is used. If the gangue is sand or quartz, SiO_2, as it usually is, the flux used is $CaCO_3$; if the gangue is $CaCO_3$, as it sometimes is, a flux is used containing SiO_2. The flux unites with the infusible earthy matter, or gangue, to form a glassy, fusible substance, called *slag*. When the charge reaches the boshes, we have, supposing the flux to be limestone, CaO (from $CaCO_3$ by heat), Fe_2O_3, (or FeO if the ore is $FeCO_3$), coal and gangue. Near the top of the hearth there are several openings through which a blast is introduced, conducted through pipes called *tuyeres*. The nozzles of the tuyeres are protected from the intense heat by sheaths, through which water circulates. It has been found economical to heat the blast, and for this purpose the waste heat of the furnace is conducted into a brick chamber. The blast is then passed through the heated chamber. Two chambers are commonly used, and while one is heating the blast, the other is being heated by the waste heat. The great volume of air introduced makes the fire burn very intensely. At the mouth of the blast the air combines with the coal, forming CO_2.

$C + O_2 = CO_2$. (At the mouth of the blast).

In passing up through the heated coal in the boshes, the CO_2 becomes further carbonized, forming CO.

$CO_2 + C = 2CO$. (In the boshes.)

CO is an inflammable gas and is a powerful reducer. The pale blue flame characteristic of hard coal fires is the CO absorbing O from the air to form CO_2. In the blast furnace the CO passing up through the shaft draws the O from the ore, reducing the oxides to the metal. The reduction takes place mostly in the boshes.

$Fe_2O_3 + 3CO = 2Fe + 3CO_2$. (In passing up the shaft.)

But Fe is the least fusible of the common metals, so that it would solidify at the mouth of the boshes and choke it up. But the iron combines with the intensely heated coal, forming a carbide of iron, which is fusible and passes down. Melted iron is the only substance that will dissolve C. This carbide of Fe is cast iron. Meanwhile the heat has caused the flux to combine with the gangue, and the slag floats on the surface of the molten iron like oil upon water. The iron collects at the bottom in the crucible, and is prevented from flowing off by a dam. When sufficient iron has collected, the slag is let off over the dam, and the iron through a hole in the dam. The melted iron is run into channels made in the sand, and allowed to cool. The main channels are called "sows", and the smaller ones branching off from them, "pigs." This iron is called pig iron. Various plans have been formed to utilize the slag which accumulates about an iron works. It has been tried, not very successfully, as a building stone. It is used for packing steam pipes, in fibres like asbestos; the fibres are formed by passing steam through melted slag. Blast furnaces are from 40 to 90 ft. high. When once started they are run continuously, as, if allowed to cool, the mass solidifies and has to be cut out with a cold chisel. This is more expensive than building a new furnace would be. There are three varieties of cast iron; white, gray, and mottled. (1) White iron is brittle and has a crystalline fracture. In this variety all the C is chemically combined with the Fe, and there is more C in it than in any other variety. Mirror iron, or "spiegeleisen," is a well crystallized white iron containing a very large amount of C. (2) In the gray iron only a part of the C is chemically combined. It is at first all combined, but afterwards separates out, forming minute plates of graphite. It has a granular structure. the crystals being coarser than those of white iron. (3) Mottled iron is a mixture of gray and white iron. White iron has about 5.8% of C, all combined, and is too brittle for castings; gray iron has about 1.8% of C combined, and 3.8% free. It is the variety usually chosen for castings. Mottled iron is too tough for ordinary castings, but is used for large cannon. Cast iron is probably a mixture of Fe and Fe_4C in varying proportions.

Wrought Iron. Puddling Process. Mottled iron, although the toughest variety of cast iron, is not tough enough to be worked. For this purpose wrought iron is used. This is nearly pure iron, very tough and infusible, as has been said. It can be extracted directly from the ore by the Bloomery process, but this is expensive and not much used. As a rule wrought iron is made from cast iron by burning off the C in a puddling furnace. The variety of cast iron commonly used is white iron; gray and mottled iron are not used, as it would be hard to burn off the graphite, which is very infusible. Gray and mottled iron, however, may be converted to white iron by the Finery process, and then put into the puddling furnace. The puddling furnace is similar to a reverberatory furnace, except that it has doors in the sides for the admission of air. Pigs of iron are laid on the hearth of the furnace and heated. The air let in burns off the C. The impurities P, S, and Si, the presence of which makes the iron much more brittle, are also burned off. The P and S, especially, impair the strength of the iron. Si is present in considerable quantities, but it is not so injurious. The products of the combustion are SO_2, CO, SiO_2, and P_2O_5. CO, a gas, passes off. The heat is so great that part of the iron burns, forming Fe_2O_3. This Fe_2O_3 combines with the SiO_2 to form slag, or ferric silicate. The slag then absorbs P_2O_5

and SO_2. Sometimes Fe_2O_3 is added to the cast iron in the beginning, to help furnish O.

$$2Fe_2O_3 + 3Fe_4C = 16Fe + 3CO_2.$$

To expose fresh surfaces to the air, the mass is constantly stirred or puddled with a long iron rod. From this the whole process is called the Puddling process. This stirring is hard work and is expensive; hence numerous plans have been devised to get rid of it, but none of them have proved successful. One of these devices is a revolving floor. When the C has been all burnt off, the iron separates out in spongy infusible lumps called "Bloom." The iron must be removed as soon as formed since otherwise it would be oxidized and wasted. From time to time, pieces about as big as a man's head are raked together, pushed out of the end of the furnace with a pole, and taken to a press, where the slag in their pores is squeezed out. The iron is then taken to the trip-hammer and hammered. The particles of iron unite and become welded together into a bar of almost pure iron. The bars are next passed between a succession of rollers, each pair having a smaller space between them than the preceding. In rolling, each particle of the iron is drawn out to a thread, giving the rolled iron a fibrous structure. Owing to its fibrous nature, wrought iron is tough and has a hackly fracture. To obtain the finest iron, the bars are cut up, bound together in bundles, and these bundles of fagots are put into a reheating furnace. This is like a reverberatory furnace, except that the bridge is very high, and, as the air has to pass through a large amount of heated coal, the iron is in an atmosphere of CO_2 and N, so that no oxide is formed. After heating, the bundles of fagots are removed, hammered, and rolled into a single bar. This iron is tougher than when treated only once.

Steel. In composition, steel lies between cast and wrought iron. Cast iron has from 2% to 5% of carbon, while wrought iron has less than 1% of all impurities. Steel has from .7% to 1.7% of carbon, the best having about 1.3%. To obtain steel, we can remove carbon from cast iron or add it to wrought iron. By the first method, we can take iron out of the Puddling Furnace before all the carbon has burned off. But it is very hard to hit the point when just enough carbon is left in the iron. There are two ways of adding carbon to wrought iron, the Bessemer Process and the Cementation Process. The *Bessemer Process* was invented to take the place of the Puddling Process in making wrought iron. The essential part of the apparatus is an iron converter, lined with infusible clay and mounted on hollow trunnions. A charge of melted white iron is put into the converter and the blast turned on. The blast enters through the trunnions, passes down between the lining and the outside of the converter, and bubbles up through holes in the bottom, burning off the carbon very fast. When the carbon is all oxidized, as indicated by the changed color of the flame, the blast is turned off. The heat here is tremendous, keeping the ordinarily infusible wrought iron in a continual state of fusion. Bessemer hoped now to pour off the wrought iron, but the phosphorus and sulphur are not burned off, so the iron would not be good. To make steel, just enough mirror iron is put in to give the required per cent of carbon. The blast is turned on a minute to make the mass homogeneous, and then the steel poured out and cast. This steel is not good enough for fine work, as it contains most of the impurities of the cast iron. It is used for rails, plows, and rough purposes. *Cementation Process.* Bars of wrought iron are packed in boxes, surrounded by Cement Powder consisting chiefly of charcoal. The bars are heated to a cherry red heat but not enough to fuse, so that we have the solid iron and carbon. The surface of the iron combines with carbon, and the carbon is transferred from particle to particle through the whole mass. The process occupies about 8 days. The bars become covered with blisters and are therefore called Blistered Steel. The structure changes from fibrous to crystalline, and the steel has a crystalline fracture, whereas the wrought iron had a hackly fracture. The steel is not yet homogeneous. To become homogeneous, it has to undergo another process. It can be melted and cast, becoming Cast Steel; or the fagots of blistered steel can be bound into bundles, heated, and welded together with the trip-hammer. This process is called tilting and the steel is called Tilted Steel. The great value of steel lies in its property of allowing *tempering*. If steel be heated to redness and suddenly cooled, it becomes very hard and brittle. This kind of steel is used for files. A watch spring, however, is soft and elastic. To get the different grades of hardness, the hardened steel is reheated and the changes of color which the metal takes on are noted. These colors are due to the formation of oxides and correspond to different degrees of hardness. The reheating may be done in a fire or in a bath of melted metal. At 200° the color is a pale straw yellow, and this temperature has been found to give the hardness needed for lancets and razors. At higher temperatures the color grows deeper. The full yellow is the best for pen-knives, purple for table-knives, blue for watch springs and swords. Damascus blades are covered with fine wavy lines, as each one is made of many bars welded together. Wrought iron can be hardened by heating it with carbon for a short time, thus covering it with a thin layer of steel. This is called case hardening.

IRON, Fe. Wrought iron is very nearly pure, but a purer iron can be got by reducing Fe_2O_3 by hydrogen. This iron is in a fine powdery form and will burn like tinder. Iron is a white metal, rather hard, and very infusible. Its sp. gr. is 7.7. It is the toughest metal known and can be drawn into very fine wire. The purer iron is, the more ductile it is, and the purity of Fe may be tested by the fineness of the wire that can be drawn from it. Iron is magnetic; cast iron however is not. Pure iron takes and gives up magnetism very easily, but steel neither assumes nor gives it up so readily; so wrought iron forms temporary magnets, while steel forms permanent magnets. Of the minerals containing iron, magnetite is in many cases naturally magnetic, while neither haematite nor iron pyrites are magnetic. Weak HNO_3 readily dissolves iron, but strong HNO_3 causes it to lose certain chemical properties and assume a passive condition. If we dip iron changed in this way by strong HNO_3, into a solution of $Cu(NO_3)_2$, it is unchanged; but if we then scratch ever so lightly the surface of the iron, it immediately turns yellow. The reason is this: a layer of ferric nitrate is formed by HNO_3 upon the iron, which prevents the $Cu(NO_3)_2$ from acting; but the scratch opens a way for it, and metallic copper is at once deposited all over the surface of the iron. Iron filings burn with scintillations and hence are used in Roman candles and other fireworks. Iron rusts on exposure to the air, forming this hydrate. This rust, unlike the rust of Zinc, eats in until the iron is all consumed.

There are two principal classes of iron compounds; ferrous, as FeO, where Fe is bivalent; and ferric, as Fe_2O_3, where Fe_2 is sexivalent, Fe being probably quadrivalent. The ferrous compounds correspond to compounds of Zn, as ZnO; and the ferric, to compounds of Al, as Al_2O_3. The two classes are about equally stable, but in air ferrous pass easily to ferric compounds, because the air contains O. Any oxidizing agent will convert ferrous compounds to ferric, and a reducer will reverse the change. Ferrous salts therefore cannot be kept in solution. The simplest form of the reaction for converting a ferrous to a ferric salt would be,

$$2FeCl_2 + 2HCl + O = Fe_2Cl_6 + H_2O.$$

The O can be supplied by HNO_3 or any other oxidizer. A ferric salt can be converted to a ferrous by boiling it with Zn or Fe.

$$Fe_2Cl_6 + Zn = 2FeCl_2 + ZnCl_2.$$

A better way is to use nascent hydrogen.

$$Fe_2Cl_6 + Zn + 2HCl = 2FeCl_2 + ZnCl_2 + 2HCl.$$

The HCl dissolves the Zn, forming $ZnCl_2$ and setting free hydrogen. This nascent H removes Cl_2 from Fe_2Cl_6, forming HCl. Besides the above classes of compounds, there is a third, the ferroferric, corresponding to the oxide Fe_3O_4.

I. FERROUS COMPOUNDS. *Ferrous oxide*, FeO, is black and unstable. *Ferrous hydrate*, FeO_2H_2, can be made by adding KOH to a soluble ferrous salt. When pure, the hydrate is white, but if the least trace of O be present, it turns first green and then red, becoming ferric hydrate. *Ferrous sulphide*, FeS, is made by adding $(NH_4)_2S$ to a soluble ferrous salt. If we add $(NH_4)_2S$ to a ferric salt, we also get FeS, for since H_2S is a reducer it reduces the ferric compounds to ferrous.

$$Fe_2Cl_6 + H_2S = 2FeCl_2 + 2HCl + S.$$

FeS may also be made by heating together sulphur and iron. It is soluble in acids, insoluble in water and alkalies. Its chief use is in the preparation of H_2S, for when treated with a strong acid this reaction takes place.

$$FeS + H_2SO_4 = H_2S + FeSO_4.$$

FERROUS SULPHATE, $FeSO_47H_2O$ (green vitriol). This is one of a series of compounds called vitriols, which all crystallize in the same form with $7H_2O$. The following are vitriols formed from elements hitherto treated: $ZnSO_47H_2O$ (white vitriol), $MgSO_47H_2O$, $MnSO_47H_2O$, $CrSO_47H_2O$. All compounds of this class form double sulphates with NH_4 and K, *e. g.* $FeSO_4(NH_4)_2SO_46H_2O$, in which the $(NH_4)_2SO_4$ replaces one molecule of H_2O. The green color of $FeSO_4$ is characteristic of all soluble ferrous salts. Green vitriol is made by dissolving Fe or FeS in H_2SO_4, or by allowing the variety of FeS_2 known as marcasite or white iron pyrites to weather, or oxidize in the air. Like all ferrous salts, $FeSO_4$ passes easily to the ferric. This change takes place gradually on exposure to air; it takes place at once, however, with HNO_3.

$$2FeSO_4 + H_2SO_4 + O \text{ (from } HNO_3) = Fe_2(SO_4)_3 + H_2O.$$

The solution has a dark color, because NO from the nitric acid unites with the excess of $FeSO_4$, forming a black compound. Upon heating, this black compound decomposes, NO is given off, and the black color disappears. Owing to the formation of this black compound, $FeSO_4$ is used as a test for HNO_3 or a nitrate. *Uses:* the readiness with which ferrous sulphate passes to ferric, leads to several important uses. When $FeSO_4$ is mixed with tannic acid (from nutgalls) it forms ferrous tannate, soluble and colorless, which on exposure to air becomes ferric tannate, insoluble and black. This ferric tannate can also be formed from $Fe_2(SO_4)_3$ and tannic acid. Ferric tannate suspended in water is used as a black ink, but, as it is insoluble, the ink is liable to become muddy. "Writing fluid" is a solution of ferrous tannate, with indigo added to give color. On being exposed to air, the writing turns black, owing to the change to ferric tannate. In tanning, the $FeSO_4$ unites with the tannic acid in the leather, forming ferrous tannate, which turns black on exposure to air. The use of $FeSO_4$ in dyeing black depends on the same principle. $FeSO_4$ is a valuable reducer; it reduces potassic permanganate. [See under $K_2Mn_2O_8$]. Fuming Sulphuric acid, $H_2S_2O_7$, can be made from ferrous or ferric sulphate. Ferrous sulphate is also used as a disinfectant. It has an acid reaction, since Fe is a weak basic radical.

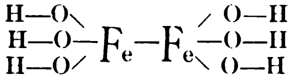
Ferrous Carbonate, $FeCO_3$, is made by adding a soluble carbonate to a soluble ferrous salt. It is insoluble in water, and white, but on exposure to air it turns to ferric hydrate, becoming black. Like $CaCO_3$, it dissolves in water containing CO_2, forming iron temporarily hard water called Chalybeate water. This is a valuable tonic. When such water is exposed to air, it gives off CO_2, and deposits $FeCO_3$, which passes to the hydrate, forming Bog Iron Ore. These deposits usually occur in swamps and marshes containing decaying organic matter which gives CO_2 to the water.

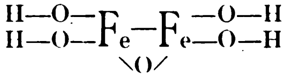
II. **Ferric Compounds. Ferric Oxide**, Fe_2O_3, occurs in nature as red chalk and red ochre. It is a valuable pigment, and is used to give a red or yellow color to glass and porcelain, while FeO colors glass green, as seen in junk bottles. It can be made from ferrous sulphate, by heating it to a high temperature. When made in this way it is called rouge, and is very hard, as are most other oxides having a similar formula, *e. g.* Al_2O_3. Rouge is used for polishing glass, silver, etc.

Ferric Hydrates. These are formed by adding NH_4OH or NaOH to a soluble ferric salt.

$$Fe_2Cl_6 + 6NH_4OH = Fe_2O_6H_6 + 6NH_4Cl.$$

The $Fe_2O_6H_6$ precipitated is gelatinous, like $Cr_2O_6H_6$ or $Al_2O_6H_6$. On heating, it parts with its water, becoming successively $Fe_2O_5H_4$, $Fe_2O_4H_2$, and Fe_2O_3. Al and Cr also have similar hydrates. The graphical formulas of $Fe_2O_6H_6$ and $Fe_2O_5H_4$ are as follows:



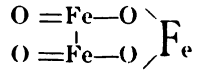


Soluble ferric salts are used as mordants in calico printing. Ferric hydrate is precipitated from them in the fibre of the cloth, and unites with the dye, modifying its color. Iron rust is merely a ferric hydrate, and occurs in nature as limonite, or yellow ochre. *Ferric sulphate*, $Fe_2(SO_4)_3$, is slightly soluble in water and, like $Al_2(SO_4)_3$, is white and forms an alum, *e. g.* $(NH_4)_2Fe_2(SO_4)_4 24H_2O$, iron-ammonia alum. This crystallizes in octahedra, and is of a light purple color. *Ferric nitrate*, $Fe_2(NO_3)_6$, is violet. *Ferric chloride*, Fe_2Cl_6, is yellow or yellowish brown and is an important laboratory reagent. It is made from ferric hydrate and HCl.

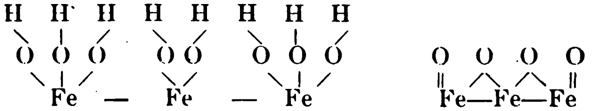
$$Fe_2O_6H_6 + 6HCl = Fe_2Cl_6 + 6H_2O.$$

In general, insoluble ferrous salts are white, soluble ferrous salts are green. Ferric salts are yellow, light purple, or reddish brown.

III. FERRO-FERRIC COMPOUNDS. *Magnetite*, Fe_3O_4, is the most important of these. One theory of the formation of this oxide is that it is a mixture of the oxides FeO and Fe_2O_3; this, however, is probably incorrect. Another theory would make it a ferrous salt of an acid $H_2Fe_2O_4$, derived by replacing the H_2 by Fe. The graphical formula would then be.



But the graphical formula of the corresponding hydrate $Fe_3O_8H_8$ could not be written. This hydrate is formed by adding KOH to a mixture of a ferrous and a ferric salt. It is probable that the graphical formulas of $Fe_3O_8H_8$ and Fe_3O_4 are as follows:



The hydrate, $Fe_3O_8H_8$, is black. The other ferro-ferric compounds are not very important. *Vivianite*, the "green sand" of New Jersey, is a ferro-ferric phosphate; it is used as a manure.

POTASSIC FERRATE, K_2FeO_4, is assumed to be formed from an acid, H_2FeO_4, although neither the acid itself nor the corresponding oxide, FeO_3, have been isolated. It is red, soluble in water, insoluble in alkalies, and is used as an oxidizer.

Fe belongs to the eighth series, but the oxide FeO_4, which we should expect, is not known, and very likely does not exist.

IV. FERRO-CYANIDES. These contain Fe, some other basic radical, and the compound radical CN, cyanogen. As NH_4 resembles K, so CN resembles Cl. Therefore we have the acid HCN, analogous to HCl. CN is univalent, and in writing its graphical formula, N may be taken either trivalent or quinquivalent, thus:

$$-C\equiv N \qquad C\equiv N-$$

Both these forms are known. The acid, when its H is united to the N, is much more violent and has a stronger smell than when the

H is united to the C. HCN is called *prussic or hydrocyanic acid.* It is a weak acid, while HCl is a strong acid. It is made by dissolving potassic cyanide, KCN, in H_2SO_4. It is the most poisonous substance known, and its salts are all poisonous. One drop is sufficient to cause instant death. The vapor, when inhaled in small quantities, renders a person insensible, when in large quantities, it causes death. Ammonia cautiously inhaled is the antidote. The odor and bitter flavor of HCN are detected in peach blossoms, kernels of peach stones, and in leaves of wild cherry. *Cyanogen*, $(CN)_2$, is a gas corresponding to Cl_2; it burns with a flame the color of peach blossoms. It is made by heating mercuric cyanide, $Hg(CN)_2$, and collecting the product over mercury. *Potassic cyanide*, KCN, is the most important salt of HCN. It is white, nearly as poisonous as HCN, and must be handled with great care, since it is liable to enter the circulation through scratches on the skin. Cyanides of many other radicals may be prepared by adding KCN to a neutral or slightly acid solution of a salt of the radical.

$$AgNO_3 + KCN = AgCN + KNO_3.$$

AgCN gives a white precipitate. If an excess of KCN be added, the precipitate redissolves, forming a double salt, AgCNKCN. The formation of double cyanides with the heavier metals is very characteristic of KCN. They are all poisonous. Upon adding an acid, as HCl, to AgCNKCN, HCN is set free.

$$AgCNKCN + 2HCl = AgCl + KCl + 2HCN.$$

Upon adding KCN to a soluble ferrous salt, we get $Fe(CN)_2 4KCN$, a salt apparently like AgCNKCN; but, upon adding to it an acid, no HCN is given off; a white precipitate which rapidly turns blue is formed. This is an acid, $H_4Fe(CN)_6$, and it is better, therefore, to regard the salt formed above, not as a double salt, but as a salt of this acid, with the formula $K_4Fe(CN)_6$. This acid is called *hydroferrocyanic acid;* it is readily soluble in water, and is white, but it is easily oxidized to another substance, which is blue.

Potassic Ferrocyanide, $K_4Fe(CN)_6$, called yellow prussiate of potash, is usually made by heating together iron, potassic carbonate, and animal charcoal containing C and N.

$$K_2CO_3 + 4C + 2N = K_2 + 3CO + 2N + 2C$$
$$= 2KCN + 3CO.$$

The K formed in the first stage, while nascent, unites with the C and N, forming KCN. It is possible to use the N of the air, but the substances have to be heated so high that it is cheaper to use animal matter. This is in the form of animal charcoal, made from old boots, blood, bones etc. Iron filings are added before heating. The KCN acts upon the Fe, forming $K_4Fe(CN)_6$. The products are dissolved, filtered, and the ferrocyanide crystallizes out in yellow crystals. From this salt all the other cyanides are made, even KCN itself; this is made by heating the ferrocyanide.

$$K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2.$$

$K_4Fe(CN)_6$ is used in case-hardening. The iron plate to be hardened is heated to a red heat and sprinkled with $K_4Fe(CN)_6$. This breaks up as above, but the C, instead of uniting with the Fe of the $K_4Fe(CN)_6$, combines with the iron plate, forming on the surface a thin layer of steel.

PRUSSIAN BLUE, ferric ferrocyanide, $(Fe_2)_2(Fe(CN)_6)_3$, was accidentally discovered in 1704 by Diesbach, while he was trying to get the color carmine. It is formed whenever $K_4Fe(CN)_6$ is added to a ferric salt.

$$3K_4Fe(CN)_6 + 2Fe_2Cl_6 = (Fe_2)_2(Fe(CN)_6)_3 + 12KCl.$$

It is used as a pigment and as a dye. The cloth to be dyed is dipped in a solution of a ferric salt, and afterwards in a solution of $K_4Fe(CN)_6$, which precipitates Prussian blue in the fibre of the cloth. This is a common method of dyeing woolens and silks. The coarser variety of Prussian blue is known as Berlin blue; the finer variety is called Paris blue. Prussian blue is insoluble in water and all acids, except oxalic acid. Dissolved in oxalic acid it forms one of the best blue inks. It dissolves in KOH, forming ferric hydrate and potassic ferrocyanide.

$$(Fe_2)_2(Fe(CN)_6)_3 + 12KOH = 2Fe_2O_6H_6 + 3K_4Fe(CN)_6.$$

On account of the characteristic color of Prussian blue, $K_4Fe(CN)_6$ is used as a test for ferric salts. With a ferrous salt the precipitate formed should be white, but it is usually slightly blue from the presence of some ferric salt. Cupric ferrocyanide, $Cu_2Fe(CN)_6$, is insoluble and reddish brown. Zincic ferrocyanide is white. All ferrocyanides in fact are white, except cupric and ferric.

Potassic Ferricyanide, $K_6Fe_2(CN)_{12}$, called red prussiate of potash, is made by passing chlorine through a solution of $K_4Fe(CN)_6$.

$$2K_4Fe(CN)_6 + Cl_2 = K_6Fe_2(CN)_{12} + 2KCl.$$

It is soluble, and crystallizes in dark red crystals. We may regard it as a double salt, consisting of KCN and ferric cyanide, $Fe_2(CN)_6$, like Fe_2Cl_6; but the best way to look at it is as a salt of *hydroferricyanic acid*, $H_6Fe_2(CN)_{12}$. This acid may be formed from it by adding an acid, as H_2SO_4. *Hydroferricyanic acid* is brown, readily soluble in water, and is converted by reducing agents to hydroferrocyanic acid.

Turnbull's Blue, $Fe_3\ Fe_2(CN)_{12}$, is formed by adding $K_6Fe_2(CN)_{12}$ to a ferrous salt. It is blue and insoluble, and is used as a test for ferrous salts. Later researches seem to show that it is the same substance as Prussian blue, but the evidence is not conclusive. Potassic sulphocyanate, KSCN, when added to a ferric salt, forms a deep blood red solution (no precipitate).

$$Fe_2Cl_6 + 6KSCN = Fe_2(SCN)_6 + 6KCl.$$

This forms a second good test for ferric salts. It is an exceedingly delicate test, much more so than the Prussian blue test. For ferrous salts there is but one good test, *i. e.* Turnbull's blue.

Tests for Fe.

$K_4Fe(CN)_6$ + ferric = Prussian blue.
" " + ferrous = White (usually light blue from ferric salt.)
$K_6Fe_2(CN)_{12}$ + ferric = Brown solution.
" " + ferrous = Turnbull's blue.
KSCN + ferric = Blood red solution.
" + ferrous = No effect.

Cobalt. Co, at. wt. 58.8, was discovered in 1733 by Brandt. It got its name from Kobold (an evil spirit), because when an ore of it, smaltine, was found and thought to be an ore of silver, no silver could be extracted from it, and the Kobolds were thought to be the cause. Co occurs in various ores, usually as an arsenide, as *smaltine*, $[CoNiFe]As_2$, and *cobaltine*, $Co[S_2As_2]$. Smaltine has the white lustre of silver. Co is a little more common than

Sr, about as common as Ba, and is extracted from the ore by roasting off the As and S. By roasting the ore, sometimes with coal, we get Zaffre, an impure CoO, which is used as a source of other Co compounds. The metal cobalt, when pure, is white, hard, magnetic, and looks like polished iron. It is usually of a gray color due to the oxide. The purification of Co from its ores is very complex. The metal has no uses.

Cobalt has the oxides CoO, cobaltous oxide, of a gray color, Co_2O_3, cobaltic oxide, black and insoluble, and Co_3O_4, cobaltous cobaltic oxide, black. $Co_2O_6H_6$, black, and Co_2O_3 are about the only cobaltic salts that we have. There are a few others, but they have not been studied much. In the fourth row of Mendelejeff, as the quantivalence of an element increases, its attraction for other elements decreases, and its compounds become less stable.

COBALTOUS SALTS. The prevailing color of soluble cobaltous salts is red; of insoluble salts, pinkish white. [See corresponding distinction in ferrous salts.] CoO_2H_2 is of a rose color. *Cobaltous sulphate*, $CoSO_47H_2O$, is red and resembles $FeSO_47H_2O$. Like ferrous sulphate it is a vitriol and forms a double sulphate with NH_4, $CoSO_4(NH_4)_2SO_46H_2O$. It crystallizes well and in the same shape as the other vitriols. *Cobaltous chloride*, $CoCl_2$, is soluble in water. When crystallized with water it has pinkish red crystals, but when the water is driven off it turns deep blue. On account of this peculiarity, $CoCl_2$ is used for sympathetic ink. If we write with a solution of $CoCl_2$ on pink paper, the writing is invisible; but when the paper is heated, the water of crystallization is driven off, and the writing turns blue. A flower barometer is made in this way. On a damp day the flowers are pink, and on a dry day, blue. This leads to the consideration of the blue Co compounds. Cobalt glass is made by fusing CoO with glass. This is the best blue for glass and porcelain; in porcelain it can be used under the glaze. *Smalt* is a silicate of Co and K, prepared by fusing partially roasted Co ore with powdered quartz and potassic carbonate. A deep blue glass is thus formed, while the mixed arsenides of Ni and Fe fuse and collect at the bottom in a metallic mass called speiss. The glass, when hot, is poured into cold water, which causes it to crack up. It is then ground fine under granite stones, and put in water. The coarser settles first; thus different grades of fineness are obtained and consequently different shades of color. Smalt is used as a pigment, to color wall paper, and as a blueing; but ultramarine, on account of its comparative cheapness, has replaced it to a great extent. Another blue pigment is called cobalt blue, or Thenard's blue. It is made by heating Al_2O_3 with CoO, or with the nitrate, $Co_2N_2O_6$. This is an intensely blue substance, and is a great favorite with artists as a blue paint. The composition of Thenard's blue has not yet been satisfactorily determined. If, instead of Al_2O_3, ZnO be used, the result is a brilliant green substance, called Rinman's green. *Cobaltous nitrate*, $Co(NO_3)_2$, is a deliquescent salt, and is used as a test in the blow-pipe. When moistened with $Co(NO_3)_2$, and ignited in the blow-pipe, many compounds of Mg give a pale pink residue, those of Zn a green, and those of Al a blue. If cold KOH be added to $Co(NO_3)_2$, a blue precipitate is formed; if boiling KOH be added, the precipitate is red. The blue precipitate is a basic salt, the red is CoO_2H_2. *Cobaltous sulphide*, CoS, is black, soluble in strong acids, but insoluble in water and weak acids. We can get no potassic cobaltocyanide, but the cobalticyanide, $K_6Co_2(CN)_{12}$, can be got in yellowish white prisms. A convenient way of precipitating cobalt is by converting the salt to cobaltous hydrate, and then, by means of bromine, to cobaltic hydrate (black).

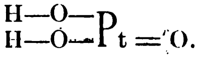
$$2CoO_2H_2 + 2H_2O + Br_2 = Co_2O_6H_6 + 2HBr.$$

Nickel, Ni, at. wt. 58.8, is more abundant than Co, and occurs associated with Fe and Co in *Smaltine*, $[CoNiFe]As_2$. The residue of this, after the manufacture of smalt, is used as an ore of Ni. It also occurs in *Kupfernickel*, Ni_2As_2. This name means "bogus copper," and was given to the ore because it looked like copper. It occurs in *Millerite*, NiS, and in magnetic iron pyrites. Meteorites are chiefly alloys of Fe and Ni. Ni was discovered about the same time as Co. The extraction of Ni from its ores is very complex, but the principle is to convert the ore to the oxide and then reduce it. For this purpose, the oxide is mixed with charcoal, pressed into cubes, and heated, leaving solid cubes of the metal. *Properties:* Ni is a hard, white, lustrous metal, very susceptible to magnetism. It does not easily rust, and may almost be classed among the noble metals. *Uses:* The chief uses of the metal depend on the fact that it has a brilliant surface and does not rust. It is used in nickel plating. This is done by decomposing with an electric current a double sulphate of Ni and ammonia. The Ni set free is deposited on the article to be plated. The process of electroplating will be more fully described under silver. Because of its great power of whitening other metals, Ni is used for alloys. The most important alloy is German silver, an alloy of brass and nickel. This is used as a substitute for silver, and is an excellent base for silver plating. Ni alloyed with copper is used for coins in the United States, Germany, Switzerland, and several other countries. The three and five-cent pieces are this alloy, and an alloy richer in copper was formerly used in the one-cent piece.

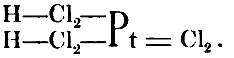
COMPOUNDS OF NICKEL. Ni has two oxides, NiO, grayish green, and Ni_2O_3, black. To these correspond the hydrates, NiO_2H_2, apple green, and $Ni_2O_6H_6$, black. Ni_2O_3 and $Ni_2O_6H_6$ are the only known nickelic compounds. Nickelous salts are characterized by their green color. *Nickelous sulphate*, $NiSO_47H_2O$ (a vitriol), is soluble, green, and forms a double salt with ammonia, which is of lighter color than the simple sulphate. *Nickelous chloride*, $NiCl_2$, like $CoCl_2$, has two colors; when crystallized with water, it is green, when anhydrous, yellow. It can therefore be used as a sympathetic ink, but it is not so good as $CoCl_2$. Nickel can be precipitated by the formation of nickelic hydrate, which is formed in the same general way as the cobaltic hydrate described above. *Nickelous sulphide*, NiS, is black. Ni forms no ammoniacal compounds like those of Co. There is no cobaltocyanide, as has just been said, nor is there either a nickelo- or a nickelicyanide. But there is a double cyanide of Ni and K, $K_2Ni(CN)_4$. The difference in the formation of the cyanides gives an easy way of separating Ni from Co. The mixture is treated with KCN, forming with the Ni the double cyanide, and with the Co, cobalticyanide. KOH is added, which breaks up the double cyanide, but has no effect on the cobalticyanide.

Platinum, Pt, at. wt. 194.3, was named from the Spanish "platina," meaning silver-like. It was discovered in 1750 by Watson, and is found in New Grenada, California, and the Ural Mountains. It usually occurs native in fine grains, alloyed with small quantities of the rarer platinum metals; sometimes it is associated with gold. It occurs chiefly in alluvial deposits. The price of Pt lies between that of gold and that of silver. *Extraction.* The alloy containing Pt is dissolved in aqua regia, a mixture of three parts HCl to one part HNO_3. To the solution, NH_4Cl is added, which precipitates Pt as ammonic chlorplatinate. Most of the other metals are left in solution, but a few are precipitated by the NH_4Cl. On heating this precipitate, NH_3 and Cl are given off, and the Pt is left in a finely divided, sponge-like form, called "spongy platinum." There are two methods of treating this spongy Pt. In Wollaston's method it is forced into iron cylinders, heated to a white heat, and forged. But the Pt thus prepared is not very good, and vessels made from it are apt to crack. To obviate this difficulty, the spongy Pt is treated according to Deville and Debray's method. It is put into crucibles lined with quick lime, fused in the oxyhydrogen jet, cast into bars and welded. *Properties:* Pt is white, very hard, fusible only in the oxyhydrogen blowpipe, with a metallic lustre. With the exception, possibly, of iridium and osmium, Pt is the heaviest metal known; its sp. gr. is 22. It is soluble in no simple acid, only in aqua regia. It is slightly attacked by NaOH and KOH, and forms with some metals, as tin, a fusible alloy. It has very weak affinities, and is not acted on by agencies in the air, *i. e.* it is one of the "noble metals." *Uses:* Owing to its infusibility, Pt is used in crucibles, but these cannot be used in fusing the alkaline hydrates, with aqua regia, or where tin or lead are set free. Pt is also used for the stills in which H_2SO_4 is concentrated; Pt, although very expensive, is cheaper than glass for this purpose, since glass breaks so easily. The experiment of using Pt for coins was tried in Russia, but it was unsuccessful, since the value of Pt is so variable. Pt has the property of condensing gases on its surface. The two finely divided forms of Pt, platinum sponge, and platinum black, have very large surfaces, and hence collect gases very readily. Platinum black is obtained by dissolving PtO in potash lye, and pouring it into hot alcohol. The Pt is precipitated in a black powder, like soot. If H be passed through the Pt sponge, it is condensed everywhere on the surface of the Pt, and burns in the O of the air. On this principle Döbereiner's lamp was constructed for striking a light, before the invention of friction matches: a jet of hydrogen was turned on to spongy Pt, and at once ignited. Likewise, if SO_2 is passed over the sponge, it will burn, forming SO_3. Platinum forms two classes of compounds, with the oxides PtO and PtO_2. The platinous compounds are of no special importance. The chloride, $PtCl_2$, is very unstable and is broken up at high temperatures.

Chlorplatinic Acid, H_2PtCl_6. The product formed by dissolving Pt in aqua regia is wrongly stated by most chemistries to be $PtCl_4$. It is really H_2PtCl_6, and it is doubtful if $PtCl_4$ has any existence. In this acid, Pt is quadrivalent. The oxygen acid corresponding to H_2PtCl_6 would be, if it existed, H_2PtO_3, like H_2CO_3. As, in the so-called sulpho acids, there is one atom of S in place of each atom of O, so in chlorplatinic acid there are two atoms of Cl in place of each atom of O. Cl, S, and O stand near one another in Mendelejeff's table. The graphic symbols of the acid and the oxygen acid are as follows:



$$\left.\begin{array}{l}H—O—\\H—O—\end{array}\right\rangle Pt = O.$$



$$\left.\begin{array}{l}H—Cl_2—\\H—Cl_2—\end{array}\right\rangle Pt = Cl_2.$$

H_2PtCl_6 when in solution is orange or yellow, but when dry it is reddish brown. (1) H_2PtCl_6 with KCl forms K_2PtCl_6, a yellow precipitate showing octahedra under the microscope, feebly soluble in water, still less so in dilute alcohol. (2) H_2PtCl_6 with NaCl forms Na_2PtCl_6, soluble. (3) H_2PtCl_6 with NH_4Cl forms $(NH_4)_2PtCl_6$, sparingly soluble. (1) and (2) are important in analysis. Na and K are extremely hard to separate, but if they both occur in one substance, all other elements are removed, and then the Na and K are converted to the chloride. On treating with H_2PtCl_6, K_2PtCl_6 is precipitated, while Na_2PtCl_6 is left in solution. The amount of K and Na can then be determined. By (3) we can obtain platinum pure, since $(NH_4)_2PtCl_6$ can be decomposed by heat, and the volatile ammonia and chlorine driven off. This leads to a method of determining the composition of organic bases. The radical NH_4 can be replaced by a univalent organic basic radical. The substance formed is weighed, and the volatile parts are driven off by heat. From the amount of the residue, the atomic weight of the radical driven off can be calculated, and its composition determined. Platinum forms many complex ammoniacal compounds.

Ruthenium, Ru, at. wt. 104; **Rhodium,** Rh, at. wt. 104; **Palladium,** Pd, at. wt. 106; **Osmium**, Os, at. wt. 195? **Iridium,** Ir, at. wt. 197. These, together with Pt, constitute the PLATINUM METALS. They are all very rare; Pt, the commonest, is a little less abundant than gold. The others usually occur with Pt and resemble it. They are all white, hard metals, with a high fusing point; Os has not yet been fused. Ru and Os have the typical oxide of the eighth series, RuO_4 and OsO_4. OsO_4 is volatile, and one of the most poisonous substances known. Rh is one of the rarest of metals. It forms a double sulphate with Na. Iridosmine, an alloy of Ir and Os, occurs with Pt, and is not soluble in any acid or mixture of acids; consequently, when Pt is dissolved from its ore by aqua regia, iridosmine remains undissolved. It is very hard and is used for tipping gold pens.

Palladium, next to Pt, is the most abundant of the platinum metals. If Palladium plates are used in the electrolysis of water, O is given off but no H. H is absorbed by the Pd until it becomes thoroughly saturated. The appearance of the Pd is unaltered but its bulk is slightly increased. Pd absorbs 900 times its own bulk of H. This property of taking up gases by a metal is called *occlusion*. Graham supposed, since the Pd becomes magnetic after the absorption of H, that this was an alloy of Pd and H; he therefore called it "hydrogenium," supposing H to be a metal. The strongest confirmation of Graham's theory came after his death. The condensation of H to a liquid was effected, and it was found to be blue, with a metallic lustre. H burns from the Pd like oil from a wick and has sp. gr. 1.5 ± in the alloy. Ni also possesses the property of occlusion. Iron is said to occlude CO, and this is offered as the explanation of the fact that CO is apt to escape from a heated stove into the room. The theory of this is that the parts of Fe next the CO unite with it, and the CO is transferred from particle to particle through the iron. At last it reaches the air, where it is set free. Somewhat similar to this property of occlusion is the condensation of H on the surface of Pt. This surface action is probably the disappearance of the property of occlusion, and both these phenomena are the dying out of the hydrides. The hydrides begin in the fourth series of Mendelejeff with RH_4, and in each succeeding series lose one atom of H, becoming in the seventh series RH. In the eighth series we should expect to find one atom of H uniting with more than one atom of these elements; but H is univalent, and so, instead of uniting with the element, it is occluded by it or condensed on its surface.

As we find in the fourth row of Mendelejeff that Fe has two cyanides, ferri- and ferro-, Co, one cyanide, cobalti-, and Ni a double cyanide; so we find in the sixth row that Ru has two cyanides, Rh one cyanide, and Pd a double cyanide. The same holds good of Os, Ir, and Pt, in the tenth row. All the metals of the platinum group form double chlorides with the alkaline metals, which are analogous to the Pt salts formed from chlorplatinic acid.

Gold, Au, at. wt. 197. Au comes in the first series, eleventh row, of Mendelejeff's table. Since the elements at the end of the even rows do not differ much from those at the beginning of the odd rows, gold should resemble Pt, and so it does. The at. wt. of Au given by Mendelejeff is 199, but it is usually given as 197, and Mendelejeff's reasons for the change are not altogether satisfactory. Gold occurs native almost universally in small quantities, especially in river sands and quartz rock. It also occurs alloyed with tellurium, and in small quantities in copper and iron pyrites. The chief localities where gold is produced are California, Mexico, Russia, and Australia. It is found in small quantities in the sands of the Rhine. Of the gold produced, America produces about one-half and Australia about one-third. Of the American yield, more than one half comes from the single state of California. *Extraction.* The sand or ground quartz in which gold occurs is washed and shaken; the sand which is lighter passes off with the water, while the gold sinks. Another method is to mix the sand or crushed quartz with mercury, and water, forming an amalgam of gold and mercury. The mercury is distilled off, leaving metallic gold. *Properties:* Gold is the only common yellow metal, and has a high sp. gr., 19.33. It is about as soft as lead, and is the most malleable and ductile of metals. To make gold leaf, a bar of gold is rolled out, placed between sheets of tissue paper, and beaten; as the leaf grows thinner, gold-beater's skin (the intestines of an ox) is substituted for the paper. Ordinary gold leaf is about $\frac{1}{170000}$ in. in thickness. If gold is coated with silver and then beaten, the silver can be removed by HNO_3, and leaves of gold obtained only $\frac{1}{12000000}$ in. thick. Gold leaf when held up to the light is transparent. The light transmitted is green, and therefore cannot come from holes or cracks in the leaf. As gold is one of the densest metals, it is supposed that all metals, if thin enough, are transparent. Gold is the typical noble metal; it does not rust but does tarnish in the air. Rusting is the formation of the hydrate, carbonate, or oxide; tarnishing is turning black by the action of H_2S or Cl. Gold is not readily acted upon by chemical agents, but it is dissolved by aqua regia. It is from this that aqua regia derives its name, gold being called the king of metals. Its melting point is 1100°. *Uses:* The chief uses are in dentistry, gilding, and for coins and jewelry. For coins and jewelry pure gold is too soft, and so silver or copper is added as an alloy. The United States and France use an alloy of one part copper to nine parts gold. In England the usual alloy is one part copper to eleven parts gold. Gilding on woodwork and plaster of Paris is done by cementing the gold leaf on with gold size, chiefly albumen; on metals it is done by electrogilding.

COMPOUNDS OF GOLD. Gold forms two classes of compounds: the aurous, as Au_2O, $AuCl$, and the auric, as Au_2O_3, $AuCl_3$. *Auric chloride*, $AuCl_3$, the most important compound, is orange yellow, crystalline, and is used in photography. It is decomposed by gentle heat. The great instability of compounds of gold is their most important property. $FeSO_4$ in passing to $Fe_2(SO_4)_3$ absorbs O or Cl. $AuCl_3$ is easily reduced by it to Au, in the form of a fine red powder which is used in gilding porcelain. In the middle ages this was a favorite medicine under the name of potable gold, but it is useless because insoluble. $AuCl_3$ added to a mixture of stannous chloride, $SnCl_2$, and stannic chloride, $SnCl_4$, gives a precipitate called *Purple of Cassius*, which varies in color from purple to brown, according to the relative amounts of $SnCl_2$ and $SnCl_4$ used. Its composition has not been determined. It is used in coloring glass and porcelain. The glass colored by it is called ruby glass, and is used in horse cars. The old theory of the color of the purple of Cassius was that it was due to metallic gold; the modern theory is that it is due to the formation of oxides. Neither is satisfactory, as the purple can be used in porcelain over the glaze, and will stand the heat of the firing. When $AuCl_3$ is mixed with KCN in solution, auric cyanide, $Au(CN)_3$, is precipitated; this afterwards redissolves, forming the double cyanide, $Au(CN)_3KCN$. A solution of this is used in electrogilding.

Silver, Ag, at. wt. 108, is one of the most abundant of the noble metals, nearly as abundant as mercury. Silver is not very widely distributed, but occurs in large amounts. It is found in Mexico, Chili, Peru, Australia, Germany, and Norway; but the United States is the most important country for silver deposits, and especially the country between the Rocky and Sierra Nevada Mountains, including Colorado and Nevada. The amount produced in these mines has cheapened the value of silver all over the world. In 1877 the U. S. yielded 46,000,000 dollars of silver, more than all the rest of the world put together. Silver is found in large quantities near Lake Superior embedded in native copper. In Europe it occurs native in wires or fibres. It is usually not mixed with so much useless material as gold. Silver also occurs in many ores. There are two classes of these ores; in the first class silver is the principal metal, while the second is the ore of some other metal in which silver occurs as an impurity. The chief ores of the first class are *Horn Silver*, AgCl, *Silver Glance*, Ag_2S, and *Ruby Silver*, either Ag_3S_3As or Ag_3S_3Sb. The chief ore of the second class is *Galena*, PbS. When crystalline, it is free from Ag; if Ag is present, it is fine-grained. PbS is one of the most important sources of Ag.

EXTRACTION. The processes of extracting Ag from its ore may be divided into two classes, corresponding to the two classes of ores. (1) *Extraction from silver ores.* This can be done either by amalgamation or by the so-called extraction processes. The theory of the *amalgamation process* is to convert the ore to metallic silver, if it is not already in a metallic state, and then form an amalgam with mercury. There are many methods of doing this, and we will take the *Washoe process* as an example. The ore is first crushed to powder by falling logs called "stamps." Water is kept running into the stamping machine, so that the ore, as soon as crushed, becomes a sort of mud, and is spattered through a sieve placed round the stamps. This mud is ground with NaCl, and thus AgCl is formed. Magistral, $CuSO_4$, is added, which in some unexplained way reduces the chloride to the metal. The product is then ground with mercury, which forms an amalgam with the silver. The sand is then washed out, and the mercury distilled off. *Extraction processes.* The principle of these is that of leaching, *i. e.* the extraction of a soluble salt from a mixture of soluble and insoluble salts. The silver in the ore, and whatever other metals are present, as Cu, Fe, are converted to sulphates. If the ore is a sulphide, this is done by roasting in the air. The mixture is then heated to get rid of the $CuSO_4$, $Fe_2(SO_4)_3$, etc., which are decomposed. Ag_2SO_4, although the compounds of Ag are generally unstable, stands a temperature high enough to decompose the other sulphates. Thus there remain in the mixture Ag_2SO_4, soluble, Fe_2O_3, CuO, etc., insoluble. By lixiviation Ag_2SO_4 in solution is obtained. To this, Cu may be added, forming $CuSO_4$ and precipitating Ag_2, or the solution may be evaporated and the Ag_2SO_4 decomposed by high heat. (2) *Extraction from lead ores.* In the lead ores silver is obtained as a secondary product, and it is profitable to work them up for silver, even when the amount is not greater than 3 oz. to a ton. The ore is reduced in tne usual way, leaving an alloy of Pb and Ag. If the proportion of Ag in the alloy is large, the process of cupellation can be applied at once; but usually the Ag must be concentrated by *Pattinson's process.* In this there is a series of caldrons, each of which is heated by a separate fire.

The principle of the process is that alloys usually melt at a lower temperature than the metals composing them. The alloy is melted in one of the caldrons; as it cools, an alloy containing less silver than before solidifies first, and as it forms is removed by perforated ladles to a second caldron. The melted alloy remaining, which is richer in Ag by the removal of the Pb, is transferred to another caldron. By repeating this process with the alloys in caldrons two and three, nearly pure Pb is finally obtained in one caldron, and in another an alloy rich in Ag. This alloy is then subjected to the process of *cupellation*. This process depends on the fact that Pb is a base metal, while Ag is a noble metal. The concentrated alloy is put into a cupellation furnace, which has a saucer shaped hearth of marl, and two tuyeres to let in air. As the air plays over the surface of the melted alloy, it combines with the Pb, forming dross, PbO. In general, two substances, one solid and the other liquid, will have an attraction for each other, *i. e.* the liquid will wet the solid, when their composition is similar. Thus water will wet glass, mercury will not. Therefore in this process the melted Ag will not wet the marl, which is an oxide, and its surface consequently will take a convex shape. The PbO, on the other hand, being of like composition, will wet the marl; so its surface becomes concave, and it flows around the sides of the silver. A hole is therefore cut in the marl close to the edge of the silver, and out of this the PbO flows. As the lead burns away, the hole is cut lower and lower, and the last traces of PbO are absorbed by the hearth. When the last of the PbO disappears, the surface of the Ag flashes out. This is very beautiful and is called fulguration.

SILVER, Ag_2, is the whitest of all the metals. Its sp. gr. is 10.56, melting pt. about 1000°. It tarnishes slightly, but does not rust, and is therefore a noble metal. The usual tarnish is the sulphide, which is blacker than the chloride. We should expect its compounds to be unstable, and so they are, except the sulphate. Melted Ag absorbs O, which, as the Ag solidifies, escapes and throws out fibres of the metal. The best solvent for Ag is HNO_3; H_2SO_4 will dissolve it, if heated. *Uses:* Pure silver has no important uses; it is soft and must therefore be alloyed. The usual alloy is Cu. In the U. S. and France the silver coins are alloyed with 10% copper; in England the per cent of alloy is a little smaller. Silver is peculiarly adapted for plate and table use. It is also used in *Silver plating*. The easiest substances to plate are brass, copper, and German silver. Steel knives have to be tinned before plating. The process of electroplating is an application of electrolysis. In a battery the acid is decomposed, and H_2 is set free at the positive, or platinum pole. If a current from the battery is passed through a vessel containing an acid, a similar decomposition takes place, but the H_2, following the direction of the current, moves from positive to negative, while in the battery it moves from negative to positive. If a salt be used instead of an acid, it will also be decomposed, and the basic radical will move in the same direction as the H_2. Only certain salts, however, will act in this way. The article to be plated is thoroughly cleaned and connected with the negative pole of the battery. A bar of silver is connected with the positive pole. The bar, together with the article to be plated, is then immersed in a bath of the double cyanide of K and Ag. Decomposition takes place, and Ag is deposited on the article to be plated. The bar of Ag dissolves, and thus the bath is kept at a constant strength. It is found necessary to use the double salt, as it deposits Ag in a coherent film, while a simple salt, as $AgNO_3$, deposits it in a loose, powdery form. The double cyanide is made by dissolving $AgNO_3$ in an excess of KCN. In silvering glass, the old-fashioned way is to coat the glass with an amalgam of tin and mercury. But now the silvering is often done by metallic silver. A solution of Ag_2O in NH_4OH is made. But Ag_2O can easily be reduced. The reducer used here is usually aldehyd, C_2H_4O, commonly made from alcohol. Aldehyd has a strong tendency to take up O and become acetic acid, $C_2H_4O_2$. Therefore when the solution is poured upon glass, silver is deposited in a firm coat, since no gas is given off. Aldehyd is very volatile, so more complex substances are often used, such as grape sugar, or milk sugar. This method of silvering mirrors is better than the amalgam method, because it can be applied to curved mirrors, is not unhealthy for the workmen, and the mirrors are brighter and more lasting. What is called oxidized silver is merely silver tarnished by NH_4Cl or K_2S_5.

ARGENTIC OXIDE, Ag_2O. Silver has the oxides Ag_2O and Ag_2O_2; but Ag_2O_2 is of little importance, and no corresponding compounds are known. Ag_2O is formed by adding a soluble hydrate (except NH_4OH) to $AgNO_3$.

$$2AgNO_3 + 2NaOH = 2NaNO_3 + Ag_2O + H_2O.$$

The brownish precipitate formed is Ag_2O and not $AgOH$, which is unknown. Ag_2O is very unstable, broken up by heat and by reducing agents. It is very slightly soluble, and its solution has an alkaline reaction. If NH_4OH is added to $AgNO_3$, we get, not Ag_2O, but a substance called fulminating silver. This is one of the most violent explosives known; a slight touch is enough to set it off. Its formula is probably Ag_2NH.

ARGENTIC NITRATE, $AgNO_3$, is the most important salt of Ag. It is prepared by dissolving Ag in HNO_3. It is the only salt of Ag readily soluble in water, and hence is used as a source of most of the other salts. It is white or colorless, crystallizes in anhydrous tables, and has a neutral reaction. Its most striking property is its instability: on this depends its chief uses. It can be fused and cast in sticks, and is then called lunar caustic. On being heated beyond the fusing point, it decomposes. If a stick of lunar caustic be touched to organic matter, it decomposes very quickly, and the O set free consumes the organic matter, while metallic Ag is deposited in its place, so finely divided that it looks black. The name lunar caustic was given to $AgNO_3$, because by the old alchemists silver was represented by the moon. Another use of $AgNO_3$ depending on its characteristic property, is as indelible ink, which is merely a solution of the nitrate. It is also used as a hair dye, the black color being due to metallic silver and Ag_2S. It is used as a medicine in epilepsy. When taken thus it accumulates in the skin and blackens it. It is important in photography, being the material from which most of the other salts used are obtained. These are argentic chloride, $AgCl$, white, argentic bromide, $AgBr$, slightly yellow, and argentic iodide, AgI, distinctly yellow. They are all insoluble in water and acids. $AgCl$ dissolves easily in NH_4OH, $AgBr$ with more difficulty, while AgI

turns white but does not dissolve. When exposed to light, AgCl turns purplish black, AgBr not quite so black, while AgI is hardly affected. Notice that these elements, Cl, Br, and I, stand in the same series in Mendelejeff's table, and that the properties vary regularly down the series. Since AgCl turns blacker than the other salts, it would seem to be the best to use in photography, but it takes too long to turn, as much as five minutes. Not until the iodide and bromide were adopted was photography an entire success.

PHOTOGRAPHY. *Collodion process.* The color of neither argentic bromide nor iodide is much changed by the sunlight, but by a slight exposure they both undergo modifications which render them more susceptible of being reduced to the metal. This change takes place instantaneously, when the substances are pure, but ordinarily it takes from a few seconds to nearly a minute. The collodion process of photography has two divisions, taking the negative and printing. (1) *Taking the negative.* A plate of glass the size of the photograph required is coated with collodion, a solution of gun-cotton in alcohol and ether. This is done by allowing the collodion to flow over the surface of the plate. The alcohol and ether are very volatile, and so a film of gun-cotton is deposited on the glass. KI and KBr, or KI alone, are mixed with the collodion, or put on afterwards. The office of the collodion is merely to hold the KI and KBr on the glass. After the collodion film has formed, the plate is put into a bath of $AgNO_3$, called the "silver bath." All subsequent operations must be carried on in a dark closet. The closet, however, may be lighted by artificial light, or by sunlight transmitted through red or yellow glass, which has no effect on the plate. In the silver bath this reaction takes place:

$$2AgNO_3 + KI + KBr = 2KNO_3 + AgI + AgBr.$$

AgI and AgBr are deposited in the collodion film. When the plate turns yellowish white, it is removed from the bath and put into the shield box. On the back of this are double doors, and in front there is a slide. When the doors and slide are closed, all light is excluded. The image of the object is projected on a ground glass plate in the camera, and the shield with the sensitive plate is put in the camera in the place of the ground glass. The slide of the shield box is opened, light falls on the sensitive plate, and thus the negative is formed. The color of the plate is scarcely changed. It is now taken to the dark room to be *developed.* For this purpose it is treated with a reducing agent, usually $FeSO_4$ with acetic acid added. The $FeSO_4$ in passing to the ferric state removes Br and I in parts where the light fell, leaving in their places metallic silver. The bromide and iodide which have not been exposed to light are not so easily reduced, and so, by stopping the operation at the right point, silver will be left only on the light parts. Pyrogallol, or pyrogallic acid, an acid made by strongly heating gallic acid, is sometimes used instead of $FeSO_4$. If now the plate were exposed to sunlight, the whole of the bromide and iodide would gradually be reduced to metallic silver; the picture must therefore be *fixed.* This consists in dissolving out the unreduced AgI and AgBr by sodic hyposulphite, $Na_2S_2O_3$. The negative is then varnished and is finished. The light parts of the object transmitted to the sensitive plate most light, and on these parts of the plate, silver is deposited. On the parts which received less light than the object, the bromide and iodide were unaltered, and therefore were washed off by the $Na_2S_2O_3$. (2) *Printing.* The salt used here is AgCl. There is no need of an instantaneous change, as there is in taking the negative, and since AgCl turns black more readily than the other salts, and is cheaper, it is more convenient to use. A sheet of glazed paper is dipped first in a solution of NaCl, and then into a "silver bath"; AgCl is precipitated on the paper. The negative is placed upon this prepared paper, which is then put into the copying frame and exposed to light. The paper turns black, wherever light falls upon it through the negative. Thus the copy, or positive, has its lights and shadows corresponding to the lights and shadows of the object. The print is taken to a dark room and *toned.* The object of toning is to remove the reddish hue which Ag has, and which is seen in some old photographs. The print is washed with auric chloride. Since gold has a weaker affinity for Cl than Ag has, metallic gold is deposited in the picture, wherever silver occurred before.

$$3Ag + AuCl_3 = 3AgCl + Au.$$

By regulating the time of toning, modifications can be obtained between purple and black. This is the principal use of $AuCl_3$. It is necessary now to get rid of the AgCl left in copying and formed in toning. This is done, as in the negative, by washing with $Na_2S_2O_3$. The washing must be done with great care, as upon it the permanency of the picture depends. The picture must then be washed carefully with pure water to remove the $Na_2S_2O_3$. *Daguerreotype.* The sensitive plate is formed by making Br and I combine directly with the surface of a silver plate. After the image is taken, the plate is brought in contact with the vapor of mercury, and an amalgam of mercury and silver is formed upon the parts affected by the light. This amalgam forms the lights, and metallic silver the shades of the picture. *Ambrotype.* The picture is taken on black glass previously treated in the usual way; metallic silver, white in comparison with the black glass, furnishes the lights of the picture. *Ferrotypes* are taken in the same way, on a plate of japanned iron. In these last three methods, no negative is employed. The *carbon process* is similar in theory to heliotyping. In it, pigments of different colors can be used, and it is therefore especially adapted to copying pictures. This process gives permanent pictures, while ordinary photographs are liable to fade or become spotted.

ARGENTIC SULPHATE, Ag_2SO_4, is white and somewhat soluble in water. Its most striking property is its stability, which is much greater than that of the other compounds of Ag. It is formed in the extraction of Ag by the leaching process. The sulphide, Ag_2S, is black, insoluble in water and acids. The carbonate, Ag_2CO_3, is white and easily decomposed.

Copper, Cu, at. wt. 63.4, is much more abundant than silver; it is one of the most abundant elements, leaving out the first ten. [See iron.] Like Ag, it occurs in definite localities. It occurs largely in Chili. In the region about Lake Superior it is found native in veins. There are many theories about the way in which native copper was formed. We find native Ag occurring with native Cu, but not alloyed with it. If, as some maintain, the Cu was deposited from a state of fusion, it would be alloyed with the Ag. The most probable theory is that it was deposited from solution by galvanic action. This theory is supported by the fact that it is found only in trap dyke sections. It occurs in ores, chiefly as an oxide, Cu_2O, as a carbonate, and as a sulphide, often mixed with other sulphides. Copper Pyrites, CuS_2Fe, is the most important of these.

EXTRACTION. The process of extraction from the sulphides is the most complex, and CuS_2Fe may be taken as an example. (1) The ore is first *roasted*, and the Fe, having a stronger attraction for O than Cu has, is oxidized, while the Cu is left as sulphide. On this continent the ore is usually roasted in heaps, in continental Europe the roasting is done in stalls, and in England and Wales it is done in a reverberatory furnace. After the roasting, there is left a mixture of ferric oxide and cuprous sulphide. The SO_2 formed was formerly allowed to escape; it is very injurious, and the country around Swansea was entirely laid waste by it. Now, however, it is used for H_2SO_4. (2) The roasted ore is ground and *melted* with sand. This may be done in a reverberatory furnace, as in England, but in America and continental Europe it is usually done in a blast furnace. The Fe_2O_3 being similar in composition to the SiO_2, or sand, unites with it to form ferric silicate, or slag, while the Cu_2S is unchanged. The Cu_2S fuses and flows off with the slag into basins; the slag being lighter collects at the top, and, when the mass is solidified, can easily be separated from the *matt* or Cu_2S. (3) and (4) As not all the iron is removed by this process, stages (1) and (2) must be repeated, sometimes more than once. In this way we finally get a nearly pure Cu_2S. (5) *Roasting and melting.* The object of this is to get rid of the S. For this purpose the matt is roasted in a reverberatory furnace. A current of air is passed over the surface, and the roasting is continued until about two-thirds of the Cu_2S is converted to Cu_2O.

$$3Cu_2S + 6O = 2Cu_2O + Cu_2S + 2SO_2 .$$

The doors of the furnace are then closed, and the heat is suddenly raised; the S of the sulphide burns in the O of the oxide, forming metallic copper.

$$2Cu_2O + Cu_2S = 6Cu + SO_2 .$$

This is a general method for extracting a metal from its sulphide. As it is impossible to hit the exact point when two-thirds of the material to furnish O for burning the substance. The H_2O formed is collected by $CaCl_2$, and the CO_2 by KOH. The $CaCl_2$ and KOH are weighed, both before and after the burning, and the amount of CO_2 and H_2O formed determined.

Cupric hydrate, CuO_2H_2, is formed by adding NaOH to cupric sulphate or any other soluble salt of Cu. If two little NaOH is added, a basic salt is formed, which is green; but if the NaOH is in excess, the hydrate is precipitated, blue and insoluble. This hydrate is unstable, and upon heating turns black, owing to the formation of a hydrate $3(CuO)H_2O$. If NH_4OH is used instead of NaOH, a green basic salt is at first formed, which dissolves, giving a deep blue solution. The formation of double NH_4 salts is characteristic of Cu, and their blue color is so intense that their formation is a test for the presence of Cu. If the nitrate is the salt to which the NH_4OH is added, nitrate of cuprammonium, $Cu(NH_3)_2(NO_3)_2$, is formed. It may be regarded as formed from two atoms of NH_4NO_3, by replacing with Cu one atom of H in each molecule, thus:

$$\begin{matrix} H-NH_3-NO_3 \\ H-NH_3-NO_3 \end{matrix} \qquad \mathrm{Cu}\begin{matrix} -NH_3-NO_3 \\ -NH_3-NO_3 \end{matrix}$$

The radical $Cu(NH_3)_2$ is called cuprammonium.

CUPRIC CHLORIDE, $CuCl_22H_2O$, is soluble, and is made by dissolving Cu in an excess of aqua regia, or by dissolving the oxide in HCl. Cu is in the same row as CO and Ni in Mendelejeff's great periods; we should therefore expect it to resemble them, and it does, but more especially Ni. One of the most striking peculiarities of the chlorides of Ni and CO is their change of color when heated. Likewise $CuCl_2$, when crystallized with water, is green but when heated it changes to brown. It can therefore be used like $COCl_2$ and $NiCl_2$ for sympathetic ink; but it is not very good for this purpose since when much heated it decomposes, leaving CuO. The flame of $CuCl_2$ is blue while that of Cu and most of its salts is green; hence $CuCl_2$ is used in pyrotechny for blue fire, and other salts for green fire.

Oxychlorides of Copper. One of these occurs in nature as Atacamite, which is the same as the rust formed on copper by salt water. It is not very important but is used as a pigment called Brunswick green.

Cupric Sulphate, $CuSO_45H_2O$ (blue vitriol), is the most important salt of Cu. The reasons for calling it a vitriol are these: A mixture of $CuSO_45H_2O$ and $FeSO_47H_2O$ containing an excess of $FeSO_4$ crystallizes with $7H_2O$ in the same form as $FeSO_47H_2O$. If, on the other hand, the $CuSO_45H_2O$ be in excess, the mixture crystallizes with $5H_2O$ in the same form as $CuSO_45H_2O$. Moreover cupric sulphate forms a double salt with K or NH_4, $CuK_2(SO_4)_26H_2O$, which crystallizes like similar salts from other vitriols with $6H_2O$. Cupric sulphate is formed by oxidizing the sulphide, or by heating Cu with H_2SO_4.

$$CuS + 4O = CuSO_4. \quad Cu + 2H_2SO_4 = H_2 + CuSO_4 + H_2SO_4$$

$CuSO_4$ is slightly efflorescent, soluble, has an acid reaction, and crystallizes in large blue crystals. The blue color is due to water of crystallization, for when anhydrous the sulphate is white. If a little water be added to the anhydrous form it is quickly absorbed, and the sulphate becomes blue. This property leads to the use of $CuSO_4$ as a test for H_2O in the laboratory. It is also good to remove the last traces of water, as from alcohol. *Uses:* One of the most important uses of $CuSO_4$ is as a source of other Cu compounds. Most of the other Cu salts are used as pigments. Arsenic green is the most valuable light green. Casselman's green is a basic sulphate. $CuSO_4$ is used in dyeing and calico printing. An important use of $CuSO_4$ is in galvanic batteries. It is used in the Daniell cell, a very important, although not the most important form of cell. The zinc plate of the battery is put into a porous earthenware cup containing H_2SO_4. This cup is then put into a glass jar filled with a solution of $CuSO_4$, and containing the inactive copper plate. When the zinc and copper plates are connected, the H_2SO_4 dissolves the zinc, forming $ZnSO_4$, and setting free hydrogen. This hydrogen passes through the porous earthenware vessel and acts upon the $CuSO_4$, giving H_2SO_4 again and setting free copper. This copper is deposited upon the copper plate, and thus no hydrogen collects upon the inactive plate. The only effect is that the copper plate grows thicker, and the battery will run till it is charged with $ZnSO_4$. The solution of $CuSO_4$ is kept at a constant strength by having crystals of $CuSO_4$ in a pocket on the Cu plate. A variation of this cell is

Cu_2S are converted to Cu_2O, this copper is always impure. In practice too little Cu_2O is formed, rather than too much, thus leaving an impurity, Cu_2S. This copper is called "blistered copper"; it is brittle, covered with black spots and little bubbles. (6) This copper is not fit to use, and must be *refined*. This is done by heating, either on an open hearth called a refiner's hearth, or in a small reverberatory furnace. A blast of air plays over the surface, until all the Cu_2S is converted to Cu_2O. To reduce the oxide, charcoal is spread over the surface of the mixture of Cu and Cu_2O.

$$2Cu_2O + C = 4Cu + CO_2 .$$

The charcoal reduces all the oxide on the surface; the process is completed by stirring the mass with a pole of green oak or birch. Hydrocarbons are given off by the heated wood, and these have such a strong attraction for oxygen that they reduce the Cu_2O to the metal. This process is called *poling*. The operation must be constantly watched, and trial lots poured off frequently. By the fracture a skilled workman can tell just when the oxide has all been reduced. If it has not all been reduced, the copper has red spots and is brittle; if the operation has been carried too far, the copper is also brittle, owing to the carbide of copper formed. When the reduction is carried just far enough, the fracture of the copper is silky and its structure homogeneous. "Rosette copper" is obtained in thin plates of a dark red color, by throwing water on the melted metal and removing the plates as they are formed. The color is due to the formation of oxides.

COPPER, Cu_2, is the only full red element. It is tough and malleable (less so than Au or Ag), and can be welded. It is hard, has a sp. gr. of from 8.9 to 7.7, and melts at about 1090°. When heated and cooled slowly, Cu becomes brittle, but if cooled suddenly in cold water, it is soft. It is a very good conductor of heat and electricity. It is one of the base metals; when it rusts in the air, a basic carbonate is formed, when in salt water, a basic chloride. This rust, like Zn rust, forms a coating on the surface of the metal, which protects it from further action; copper is therefore used for sheathing ships. If copper is held near the top of the flame in the Bunsen burner, it turns red and then black, from the oxides formed. If now it be put in the middle of the flame, the oxides are reduced again to the metal by the hydrocarbons. Owing to its permanancy, Cu is valuable for domestic purposes, but not for cooking utensils, because it is soluble in many acids, especially acetic acid (vinegar.) With this acid, verdigris is formed, which, like all soluble Cu salts, is poisonous. Pickles used to be boiled with vinegar in Cu kettles, giving them a green color. Owing to the verdigris formed, these were dangerous to eat. To avoid poisoning from the copper on the one hand, and blackening from iron on the other, wooden vats are now used. Copper is insoluble in cold H_2SO_4 and HCl, soluble in hot. Aqua regia dissolves it readily. It is hardly acted upon by strong HNO_3, easily dissolved by weak. Cu is used for coins and in electrotyping. [See under the sulphate.] Cu can be precipitated from a solution of $CuSO_4$ or any Cu salt, by putting into it a piece of Fe. "Cement water" is water in copper mines containing $CuSO_4$ from copper pyrites; the copper is precipitated by scrap iron, and is known as cement copper. Copper forms many important *alloys*. *Brass* is composed of Zn and Cu, and is yellow. Pins are brass wire coated with tin. Pinchbeck and tomback are names given to varieties of brass containing a relatively larger proportion of Cu. *German silver* is an alloy of brass and nickel. The *Bronzes* are alloys of copper and tin. The bronze richest in tin is speculum metal, containing 30%; it is used for mirrors of telescopes. Medal bronze contains only about 5% of tin. Bell metal, gun metal, gongs, and cymbals are between speculum metal and medal bronze in composition. *Aluminum bronze*, an alloy of Cu and Al, is the best imitation of gold. Copper forms two classes of compounds, the cupric, CuO, $CuCl_2$, and the cuprous, Cu_2O, Cu_2Cl_2. Cu is supposed to be bivalent in the cuprous as well as the cupric forms, and the two atoms of Cu to be united to each other thus, —Cu—Cu—.

I. CUPRIC COMPOUNDS. CUPRIC OXIDE. CuO, is black, and may be made by burning Cu in the air, or by heating cupric nitrate:

$$Cu(NO_3)_2 = CuO + 2NO_2 + O.$$

Its most important use is in organic analysis, where the object is to find the amount of C and H in a substance. CuO is the best obtained by having the outer vessel made of copper, thus itself forming the inactive plate. Another important use of $CuSO_4$ is in *electrotyping*. This consists in copying a page of type on metal, so that we can print from a solid page. The advantages of electrotyping are these: (1) The plates may be kept and the type does not have to be set up again; (2) the plates give better and sharper impressions than type; (3) any number of electrotype impressions can be made, and printing can be done from all at the same time. The page is set up in type and an impression taken in wax. The wax is coated with graphite which conducts electricity over the whole surface. The mould is attached to the negative or zinc pole of a battery, and a bar of copper at the other pole. They are immersed in a bath of $CuSO_4$, and, by the same action as in electroplating, the $CuSO_4$ is decomposed, and the copper deposited is spread evenly over the surface of the mould. The copper plate formed is made in the shape of a hollow pan, and a fusible metal is poured in to give it more stiffness. The process takes about twelve hours, and therefore newspapers, unless printed from the type itself, are usually printed from stereotype plates since it is quicker. The blue crystals of $CuSO_4$ are used in medicine as a mild caustic with which oculists sometimes touch the eye, and to preserve wood from decay, especially in railroad sleepers.

CUPRIC NITRATE, CuN_2O_6, is formed by dissolving Cu in HNO_3.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$$

It is blue and deliquescent. If we attempt to obtain $Cu(NO_3)_2$ from its solution, it is apt to break up, forming a basic nitrate. The heat must therefore be carefully regulated. The formation of basic salts is one of the most characteristic properties of compounds of Cu. The *carbonates* are really basic salts. *Malachite* (green), $CuO_2H_2\,CuCO_3$, occurs in Siberia. It is found in concentric layers, and when cut and polished is a beautiful gem; it is used for jewelry, paper-weights, table-tops, &c. *Azurite*, probably $CuCO_3 2CuO_2H_2$, is blue and used as a pigment, called mineral blue. *Verditer* is the neutral, and *Verdigris* the basic acetate. The name verdigris is often wrongly applied to copper rust. They are both green.

If $K_4Fe(CN)_6$ is added to a cupric salt, a dark reddish brown precipitate, $Cu_2Fe(CN)_6$, is obtained. This is the most delicate test for copper.

II. CUPROUS COMPOUNDS. Cu stands directly over Ag in Mendelejeff's great periods, but up to this point there have been few resemblances between the two metals. The cuprous compounds however have a strong resemblance to the argentic compounds. They are all very unstable; with the exception of the sulphide and the oxide they cannot be kept in air, but pass to the cupric salts.

Cuprous Chloride, Cu_2Cl_2, is made when $CuCl_2$ is boiled with copper.

$$CuCl_2 + Cu = Cu_2Cl_2.$$

We can make it, therefore, by dissolving Cu in excess in aqua regia. $CuCl_2$ is probably first formed thus:

$$O\ (\text{from } HNO_3) + 2HCl = Cl_2 + H_2O.$$

The Cl_2 combines with the Cu, forming $CuCl_2$. Thus the full reaction would be:

$$O\ (\text{from } HNO_3) + 2HCl + Cu = CuCl_2 + H_2O.$$

The $CuCl_2$ unites with the excess of Cu, forming Cu_2Cl_2. Cuprous chloride is soluble in strong acids, insoluble in weak, and like AgCl it is insoluble in water, soluble in NH_4OH. It is white, but when in solution in a strong acid it looks black. It turns black on exposure to the sun, like AgCl, and passes readily by oxidation to $CuCl_2$. This change takes place in the air, and more quickly with an oxidizer as HNO_3.

$$Cu_2Cl_2 + 2HCl + O\ (\text{from } HNO_3) = 2CuCl_2 + H_2O.$$

When added to NH_4OH, $CuCl_2$ dissolves, forming $Cu_2(NH_3Cl)_2$. This solution is colorless, but it oxidizes in the air, becoming $Cu(NH_3Cl)_2$, blue.

Cuprous Oxide, Cu_2O, occurs in nature as Cuprite or Red Copper. It is an important ore of copper. When Cu is heated in air, it is oxidized first to cuprous oxide (red), and then to cupric (black). The formation of Cu_2O and $Cu_2O_2H_2$ leads to an important use as a test. If CuO is added to a solution containing grape sugar, it is reduced to Cu_2O. This is somewhat similar to the action of Ag_2O with grape sugar. The principle of this forms the basis of Fehling's test for grape sugar. Fehling's solution is cupric tartrate, from $CuSO_4$ and tartaric acid, containing an excess of KOH; it is a blue solution. When it is added to grape sugar, an orange precipitate, $Cu_2O_2H_2$, is formed, which upon boiling is decomposed into H_2O and Cu_2O (red). This is a valuable test for physiologists, since grape sugars or similar sugars occur in many animal and vegetable substances. CuO gives to glass a bluish green color; Cu_2O, a red color. Cu_2S occurs in nature as Copper Glance; it is black.

Mercury, Hg, at. wt. 200, is more abundant than Ag. It is occasionally found native, but usually as a sulphide, HgS, called Cinnabar. There are only three important places where Hg is found: Almaden in Spain, the oldest, Idria in Illyria, and New Almaden in California. The ore at New Almaden was discovered only a few years ago, but now it yields more than all the rest of the world together. *Extraction*. This is simple because Hg is on the border line between the noble and the base metals; it may be considered one of the noble metals, since it does not easily oxidize. Hence the first roasting gives, not the oxide as in copper, but the metal.

$$HgS + 2O = Hg + SO_2.$$

It is only necessary to use kindling to light the cinnabar, for the heat of the reaction is sufficient to continue the combustion, and to volatilize the Hg, which therefore passes off in vapor. There are three methods for condensing the Hg vapor: (1) In Idria the vapor is passed through a succession of brick chambers and is cooled by the brick walls. Since there are many joints in the chambers, much of the vapor is lost, and it is thus found profitable, after some time, to remove the chambers and distill the walls, together with the earth under and around them. (2) In Almaden the vapor is passed through a series of Alludels on an inclined plane, and the Hg flows out at the bottom. These alludels are pear-shaped vessels of glass or earthenware open at both ends, and fitted into one another. The joints are closed by clay, but since it is impossible to make them tight, and there are so many of them, more vapor is lost than in the Idrian process. (3) In New Almaden the mercury condenses in iron tubes. This process was invented in Idria, and is the best of all, since there are fewer joints through which the Hg can escape. The only disadvantage is that the iron is corroded by the SO_2 which passes off with the Hg. The Hg is collected and sent to market in iron bottles with iron stoppers.

MERCURY, Hg, often called quicksilver, is the only metal liquid at ordinary temperatures. Its color is bluish, about like lead, and it solidifies at 40° below zero, about the point where the Fahrenheit and Centigrade scales coincide, forming soft crystals. It boils at 350°, but is slightly volatile at ordinary temperatures. The sp. gr. of its vapor is 100 referred to hydrogen, and consequently the molecular weight of Hg is 2×100, or 200. This is the same as its atomic weight, and hence Hg has one atom in the molecule. There are several other elements whose at. wt. is the same as the molecular weight, and they occur chiefly in the same series as Hg, *e. g.*, Cd, Zn, and probably Mg. Mercury vapor is poisonous and takes effect in two ways. The milder form of poisoning is called salivation, and is characterized by an excessive flow of saliva. In the worst cases the mouth swells up, eruptions break out on the tongue and mouth, the gums turn black, and the teeth drop out. The more acute form of mercury poisoning is mercury palsy. The patient loses control over his muscles, and the result is often fatal. The sp. gr. of Hg is very great, 13.59; it is next to that of gold among the common metals. As the sp. gr. of iron is only about 7, an iron cannon ball will sink only a little more than half way in the mercury. Mercury is said to have been used as a bed by some eastern princes. It is comfortable but poisonous, for a little vapor escapes even at ordinary temperatures. By grinding Hg with fat, it becomes finely divided, forming an emulsion called mercury ointment. Blue pills are mercury scattered through starch. When thus finely divided, it is dissolved more easily by the gastric juice. *Uses:* The most important use of mercury is in the extraction of gold and silver. The next important use is in physical instruments, as thermometers, barometers, etc. Almost all metals combine directly with Hg to form amalgams, except those in the eighth series; these, however, can be made to form amalgams by treating a soluble salt of the metal with sodium amalgam, *e. g.*:

$$FeCl_2 + Na_2 \, x \, Hg = Fe \, x \, Hg + 2NaCl.$$

Na amalgam is either liquid or a crystalline solid. The platinum amalgam is used by dentists for filling teeth. The most important amalgam is the tin amalgam used in "silvering" mirrors. A sheet of tin foil is spread evenly on a marble table carefully levelled. This tin foil is moistened with Hg, and the Hg is then poured on till it forms a layer a quarter of an inch thick. The edge of the plate of glass is dipped below the surface of the Hg, and carefully pushed forward so as to exclude all bubbles of air. Weights are placed on the glass, one end of the table is gently raised, and the Hg drains off. At the end of twenty-four hours the table is again inclined, and the inclination is increased from day to day till the table is vertical. It takes about a month for the amalgam to harden. It is never perfectly solid on the glass, and, when mirrors are hung a long time in one position, it accumulates at the bottom. If now the mirror be reversed, the amalgam runs down in streaks and spoils the glass. The workmen on these mirrors are exposed to Hg poison, which here usually takes the form of salivation. Mercury, like copper, forms two series of salts, the mercurous, Hg_2O, Hg_2Cl_2, and the mercuric, HgO, $HgCl_2$. Like Cu, it has a strong tendency to form basic and double salts; but, although thus closely related to Cu, it stands far away from it in Mendelejeff's table. This is one of the weak points in the classification. There are, however, some striking differences between them: salts of Hg are mostly white and crystallize anhydrous, while salts of Cu are mostly colored and crystallize hydrous. The mercuric and mercurous salts are both stable, while the cuprous salts are unstable.

I. MERCURIC SALTS. *Mercuric Oxide*, HgO, can be made by burning Hg in air, or by heating the nitrate. This forms the red modification.

$$Hg(NO_3)_2 = HgO + 2NO_2 + O.$$

The salt formed is at first black, but, as it cools, it turns red or reddish orange. Another way of obtaining the oxide is by adding KOH to the nitrate or chloride.

$$HgCl_2 + 2KOH = HgO + H_2O + 2KCl.$$

In a similar reaction with $CuSO_4$ we get CuO_2H_2 when cold, and CuO when hot; but HgO_2H_2 is so unstable that it breaks up at once, even when cold. HgO prepared in this way is yellow. The two modifications differ from one another in many properties. The yellow modification dissolves in oxalic acid, forming a white oxalate, while the red modification is not affected; the yellow modification is acted on by chlorine, forming, when slightly heated, an oxychloride of Hg, and when strongly heated, $HgCl_2$, while the red modification is not affected; the yellow modification is said to be more soluble in water than the red. A theoretical explanation of this difference is that one modification is HgO, while the other is Hg_2O_2, Hg_3O_3, or some similar form. It is impossible to decide by analysis which of these formulas is correct; the only way would be to find the sp. gr. of their vapors, but both forms are resolved by heat into Hg and O. This was the original method of obtaining O. HgO is somewhat decomposed by light. The principle of the celebrated experiment of Lavoisier, by which he proved that combustion is union with oxygen, and that air is composed of N and O, was the conversion of Hg to HgO by burning. Before the time of Lavoisier it was believed that combustion was simply the loss of an imponderable substance called phlogiston. The experiment consisted in heating mercury in a closed flask. It was found that a red substance was formed, and that, after combustion ceased, nitrogen was the only gas left in the flask. On heating the red substance, Hg was left, and a gas was evolved which proved to be oxygen. This O, when mixed with the N in the flask, made the same volume of air that the flask originally contained. This experiment was the beginning of all chemistry.

MERCURIC CHLORIDE, $HgCl_2$ (corrosive sublimate), is usually made by distilling together mercuric sulphate and common salt.

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4.$$

The $HgCl_2$ is sublimed off; to this circumstance together with the fact that it is very corrosive and poisonous, $HgCl_2$ owes it name of corrosive sublimate. It is white, crystalline, somewhat soluble in water and alcohol, with an acid reaction. It is volatile, as are all compounds of Hg which are not decomposed by heat. From its solution Hg is precipitated by Cu as a Cu amalgam. $HgCl_2$ is very poisonous; the antidote is the raw white of egg or any form of albumen, which forms with the $HgCl_2$ a compound insoluble, and hence harmless. The antidote is effective only when taken at once. The chief use of $HgCl_2$ is in medicine. If NH_4OH be added to $HgCl_2$, we get the "white precipitate" of Pharmacy. $HgNH_2Cl$ corresponds to the salts of cuprammonium. It is formed by replacing two atoms of H in NH_4Cl with Hg. Compounds of Hg have a great tendency to form double and basic salts.

Mercuric Iodide, HgI_2, is formed by adding potassic iodide to mercuric chloride.

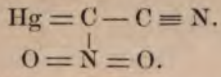
$$HgCl_2 + 2KI = 2KCl + HgI_2.$$

The HgI_2 precipitated is at first yellow, but on exposure to air, it becomes in turn salmon-colored and then a brilliant scarlet. The red modification crystallizes well, and readily dissolves in KI, forming a double salt. The scarlet modification is used as a pigment. The yellow modification is formed from the scarlet by heat, and is very unstable, easily changing back to the red.

Mercuric Sulphate, $HgSO_4$, is formed by strongly heating Hg and H_2SO_4.

$$Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2.$$

It is white, but forms with water a basic mercuric sulphate which is yellow. The basic mercuric salts are usually yellow. This sulphate, $HgOHgOHgSO_4$, is called Turpeth mineral. *Mercuric Nitrate*, $Hg(NO_3)_2$, is pure white, and is the only salt of Hg, except $HgCl_2$, that is freely soluble. It forms a yellow basic salt. *Fulminating Mercury*, $HgC_2N_2O_2$, is formed by the action of nitric acid upon alcohol and mercuric nitrate. Its formula has been determined with perfect certainty.



$$\begin{array}{l} \mathrm{Hg} = \mathrm{C} - \mathrm{C} \equiv \mathrm{N}. \\ \qquad\ \ | \\ \mathrm{O} = \mathrm{N} = \mathrm{O}. \end{array}$$

This contains the group NO_2, which is characteristic of nitroglycerine and nearly all explosives. Hg has weak affinities, and C also has weak affinities for most metals; so the Hg breaks off from the C, and the C burning in the O of the NO_2 causes the explosion. There is a similar silver fulminate, which must not be confounded with the fulminating silver mentioned under $AgNO_3$, the formula of which is probably Ag_2NH. Fulminating mercury explodes with a scratch when dry, and is used in percussion caps.

Mercuric Sulphide, HgS, like the oxide and iodide has two modifications. Cinnabar is the red modification. If H_2S be added to $HgCl_2$, a red precipitate is formed, turning black with an excess of H_2S. The red precipitate is a compound of HgS and $HgCl_2$.; the black is the black modification of HgS. The reason of the difference in color between the two modifications is probably that the red modification is crystalline, while the black modification is not crystalline. The black modification is known as Ethiops mineral, and when sublimed it gives the red modification, which is used as a pigment under the name of *vermillion*. Vermillion is also made by the moist method. In this way the black modification is mixed with some solvent, as K_2S_5, and put in a tightly corked bottle. This must be shaken for about a month. The HgS dissolves, and crystallizes out in the red modification. In China, where the best vermillion is produced, the HgS is made by rubbing together Hg and S, and the shaking is supposed to be done by hand. In this country the bottles are tied to the arm of a vertical saw in a saw mill. Vermillion is the most valuable of all pigments, and it is vermillion that gives the red color to sealing wax.

II. Mercurous Compounds. It is supposed that in these Hg_2 is a bivalent radical, like Cu_2. *Mercurous oxide*, Hg_2O, is formed by adding KOH to a mercurous salt, usually the nitrate. It is black, insoluble, and readily passes to HgO, setting free Hg.

Mercurous Chloride, Hg_2Cl_2, like Cu_2Cl_2 is white and insoluble. It is formed by adding HCl to a soluble murcurous salt.

$$Hg_2(NO_3)_2 + 2HCl = Hg_2Cl_2 + 2HNO_3.$$

A more common way of making it is by distilling $HgCl_2$ with Hg.

$$HgCl_2 + Hg = Hg_2Cl_2.$$

If NH_4OH be added to Hg_2Cl_2, a beautiful black substance, Hg_2NH_2Cl, is formed. It is from this that Hg_2Cl_2 derives its common name, calomel (καλὸς μέλας). Calomel was formerly much used in medicine, but the practice often led to salivation. The calomel was supposed to act directly, but it has been shown that it enters the circulation only by being converted to $HgCl_2$. Since it is impossible to tell how much will thus be converted and enter the system, the use of calomel has been displaced by that of $HgCl_2$, corrosive sublimate, the amount of which can be regulated with perfect certainty. *Mercurous Iodide*, Hg_2I_2, a dirty yellowish green, is insoluble in water. *Mercurous Nitrate*, $Hg_2(NO_3)_2$, the only soluble mercurous salt, is formed by treating an excess of Hg with HNO_3. When pure, it is white, but it forms a yellow basic salt.

Lead, Pb, at. wt. 207, is more abundant than copper and almost as abundant as zinc. It has only one important ore, *Galena*, PbS. This occurs in cubic crystals with cubic cleavages; it is lead gray with a slight red tint, and very brittle. *Cerusite*, $PbCO_3$, has lately come into importance at Leadville. The U. S. yield a large amount of all the lead produced. Nearly pure galena is found along the bluffs of the Mississippi river, especially at Galena, Dubuque, and in Wisconsin. Further west, particularly in Colorado, there is much argentiferous galena. The silver alone in it is enough to pay the cost of extraction, and the Pb can be sold for almost nothing. Lead is also found in the Hartz mountains, Silesia, and England. *Extraction*. There are two principal methods of extracting Pb from the ore. (1) This method is the only one applicable if the ore is mixed with sandstone or quartz, for in the other method much of the Pb would combine with the SiO_2, forming plumbic silicate, and would thus be wasted. The ore is therefore powdered, and heated with scrap iron in a small blast furnace.

$$PbS + Fe = Pb + FeS.$$

A slag is formed by the gangue and the flux used. which separates out from the Pb. (2) This is the ordinary way of extracting a metal from its sulphide. The sulphide is heated in a reverberatory or small blast furnace.

$$3PbS + 3O_2 = 2PbO + PbS + 2SO_2.$$

The doors are then closed and the heat is raised.

$$2PbO + PbS = 3Pb + SO_2.$$

[Cf. with this process, stage (5) in the extraction of copper.]

Lead, Pb, has a bluish color, a sp. gr. of 11.37, and a mpt. of 325°. It is soft, flexible when pure, tolerably ductile and malleable, but not tenacious. By the action of air a basic carbonate is formed, which protects the lead from further action. Dross, PbO, is formed on the lead when it is heated. Lead and all its soluble compounds are poisonous. *Uses:* Lead is used in making bullets. Bullets are sometimes made by pressing cold Pb, but usually by fusing the Pb, and then casting it in a mould. Shot is made by pouring melted lead, together with a little arsenic, through a sieve at the top of a high tower called a shot-tower. The arsenic makes the drops rounder and harder, but the amount is very small; otherwise the shot would be too brittle. The drops solidify in the air and fall into water. The shot is then sorted by being passed through sieves. In order to separate out those shot which are not perfectly spherical, the shot is run down an inclined plane, at the base of which are placed two boxes. The round shot acquire a velocity sufficient to carry them over the first box into the second, while the deformed ones drop into the first box. Sheet lead is made by pouring melted Pb on a table, and letting it solidify. Lead pipes are made by the "squirting" process. A hollow cylinder, in the centre of which near the top is a cylindrical iron bar, is filled with melted lead. The lead is then slowly forced through the cylinder, and solidifies as it reaches the air. Lead pipes are much used for water pipes, but the air and water together dissolve some of the lead, forming PbO_2H_2, which is slightly soluble.

$$Pb + O + H_2O = PbO_2H_2.$$

Where the surface of Pb is not large, as in a water pipe, not much of it dissolves, but yet there is a perceptible amount. Some waters affect the Pb much more than others; nitrates and chlorides increase the power of the water to dissolve Pb, while phosphates and sulphates, by forming a thin layer of phosphate or sulphate of Pb which prevents further action, decrease its power. Acid carbonates in the water dissolve the lead, forming lead temporarily hard water. The danger of lead poison is that it is a cumulative poison; it collects in the system, especially in the muscles. The form that lead poison usually takes is that of drop wrist, corresponding to mercury palsy. The patient cannot hold up his hands, and a narrow black or blue line forms on the gums. Potassic Iodide is the antidote for lead poisoning; it forms with Pb plumbic iodide, which is soluble and can be eliminated from the system. The KI must be given in small doses, since if all the Pb were converted to PbI_2 at once, so much would enter the circulation as to cause acute lead poisoning, which would be fatal. Iron water pipes are not perfectly safe, because they are soldered together with Pb at the joints; an electric current is generated between the Pb and the Fe, dissolving the lead much more quickly than if the pipe were wholly lead. A lead pipe lined with block tin is better, but if a hole is worn through the tin, the galvanic action between the Pb and the Sn dissolves the Pb much more rapidly. Brass and zinc are sometimes used; although poisonous, they are not cumulative poisons, and hence are better than Pb. An alloy of lead and tin is used as a solder.

Lead forms only one well marked series of salts, the plumbic, PbO, $PbCl_2$. It stands in the fourth series of Mendelejeff's table. It has a strong resemblance to Ba, and therefore should perhaps stand in the second series; but we find an oxide PbO_2 and a few other similar compounds.

PLUMBIC OXIDE, PbO, is the dross formed by burning Pb, and is one of the principal products in the cupellation process. It receives the name *massicot* or *litharge*, according to its form. Massicot is unfused PbO, a yellowish brown powder; litharge is crystalline and is obtained by carrying the heat so high that the Pb fuses and forms small salmon-colored scales. Both forms are insoluble in water. *Uses:* Litharge is used in making glass, for the glaze in earthenware, as a pigment, and as a source of all other Pb compounds. Plumbic hydrate, PbO_2H_2, is white, amorphous, slightly soluble in water, and soluble in KOH.

PLUMBIC PEROXIDE, PbO_2, is formed by oxidizing plumbic oxide or hydrate. The action may be represented thus:

$$PbO_2H_2 + Br_2 = PbO_2 + 2HBr.$$

PbO_2 is a chocolate brown powder used as an oxidizer. *Red Lead or Minium.* This is an indeterminate oxide made by carefully oxidizing massicot or litharge in a reverberatory furnace. Usually Pb_3O_4 or Pb_4O_5 is obtained. Each of these forms, when treated with dilute HNO_3, yields PbO_2 and $Pb(NO_3)_2$, which shows that the red lead is a compound of PbO and PbO_2 in varying proportions. Pb_3O_4 may be written $PbO_2 2PbO$, and Pb_4O_5 may be written $PbO_2 3PbO$. Red lead is shown to be a compound and not a mixture by its color; PbO_2, chocolate brown, and PbO, yellow, when mixed, could not give the optical effect of red. Red lead is used in making glass, as a pigment (not so good as vermillion), as a protective paint on iron, and with oil it forms cement for gas pipes.

Plumbic Acetate, $Pb(C_2H_3O_2)_2$, called sugar of lead, is the only common soluble Pb salt, except the nitrate. It is made by dissolving PbO in acetic acid.

$$PbO + 2HC_2H_3O_2 = Pb(C_2H_3O_2)_2 + H_2O.$$

It is white, has a sweet taste, slightly soluble in water, and, like all soluble Pb salts, has an acid reaction. It is poisonous, used as a medicine, as a lotion, and in dyeing to precipitate chrome yellow. It forms many basic plumbic acetates. Goulard's extract is the basic acetate, $PbOPb(C_2H_3O_2)_2$. It is soluble, used in medicine, and in making white lead. In all these basic acetates the radical is bivalent. Thus the radical of $PbOPb(C_2H_3O_2)_2$, corresponding to chrome orange, may be written (—Pb—O—Pb—), and the radical of $PbOPb(C_2H_3O_2)_2$ may be written (—Pb—O—Pb—O—Pb—).

White Lead. This is a basic carbonate, containing the hydrate and carbonate in varying proportions. By the *French and English methods*, the basic acetate is first made from litharge and plumbic acetate, and then CO_2 is passed through it.

$$PbOPb(C_2H_3O_2)_2 + CO_2 = PbCO_3 + Pb(C_2H_3O_2)_2.$$

The neutral acetate formed at once recombines with more PbO, and from this new basic acetate the PbO is removed as before by the CO_2, forming more $PbCO_3$. Thus the process is continuous, and the $Pb(C_2H_3O_2)_2$ serves simply as a carrier to conduct the PbO to the CO_2.

The hydrate is formed by a second reaction.

$$2PbCO_3 + H_2O = PbCO_3PbO_2H_2 + CO_2.$$

The *Dutch method* is older and apparently more clumsy, but it gives by far the best quality of lead. It is largely used on this continent.

The metallic lead is cast into buckles or coils, and put into jars containing vinegar. These jars have circular shelves at the bottom, so that the lead does not come in contact with the vinegar. The pots are buried in piles of manure or decaying organic matter. The heat given off by the decomposition volatilizes the vinegar. Vinegar is impure acetic acid, and as the vapor rises through the buckles of lead, it converts their surface to the basic acetate. CO_2 is set free by the decomposition, and this with the O of the air, entering the jar through holes, converts the basic acetate to white lead. The white lead is ground and made into cakes. It is the best of white paints, because it combines well with the oil, does not easily peel off, and has a great concealing power; but it cracks easily, is blackened by H_2S, although slowly in air, and poisons the workmen, giving lead colic. The danger is partly avoided by drinking milk, thus forming an insoluble compound with the Pb. Two other paints have been tried as substitutes, $BaSO_4$, "permanent white," and ZnO; they are not blackened by H_2S, but do not possess the same covering power, and do not combine chemically with the oil, thus peeling off easily.

Plumbic Sulphide, PbS, formed by adding H_2S to plumbic acetate, is black, insoluble in water and weak acids. *Plumbic Sulphate*, $PbSO_4$, like $BaSO_4$, is white, insoluble in water, and crystallizes in the same form as $BaSO_4$. *Plumbic Chloride*, $PbCl_2$, is white, sparingly soluble in cold water, freely soluble in hot water. It crystallizes in needle shaped crystals. *Plumbic Iodide*, PbI_2, is sparingly soluble in water, and crystallizes in yellow scales. This color is characteristic, and PbI_2 is sometimes used as a test for lead. When heated, PbI_2 becomes dark red and fuses. *Plumbic Nitrate*, $Pb(NO_3)_2$, is soluble and crystalline. *Plumbic Chromate*, $PbCrO_4$, is used as a yellow dye.

Tin, Sn, at. wt. 118, is not so abundant as lead or copper, and is therefore more expensive. The only ore is *Tinstone*, SnO_2, black. Tin was known very early; the first metallic implements were made of bronze, Cu and Sn. The mines at Cornwall, England, were worked by the Romans, and probably before their time. Tin is also found in the island of Banca, in Malacca, Saxony, and

Australia. In Australia, the most important source, tin was discovered about 1870. Tin is the only important metal not mined in the United States. Stream tin is the name given to tinstone found in alluvial deposits. Wood tin is a variety of tinstone found in Cornwall, so called from its resemblance to knotty wood.

Extraction. A mechanical method not peculiar to tin is used in separating the SnO_2 from the gangue. The principle consists in suspending a mixture of crushed ore and gangue in water; the ore, being heavier, settles first. The ore is crushed first by stamps and then by rollers. The separation can be done in three ways. (1) A mixture of the ore, gangue, and water, is poured down an inclined plane. The heavy ore settles at the top of the plane, a mixture of ore and gangue at the middle, and gangue alone at the bottom. (2) The separation can be done in a buddle. This is a box into which water flows, and at the end of which are holes at different levels, closed by plugs. When the plugs are successively removed, sand and water flow from the top hole, pure ore from the bottom, and a mixture of sand and ore from the holes between. (3) A shaking-table is sometimes used to get rid of the gangue. To convert the pure SnO_2 to the metal, it is roasted with charcoal in a blast or reverberatory furnace.

$$SnO_2 + C = Sn + CO_2.$$

The theory of this is simple, but the details are very complex. Sn is usually purified like Cu, by poling. The best variety of this tin is called block tin. The purest block tin is often heated to near the melting point, thereby becoming brittle; when dropped from a height it breaks into prisms, which come to market as grain tin.

TIN, Sn, is a white metal with a slight yellow tinge, of a crystalline structure, soft and malleable at ordinary temperatures, but brittle at very high and very low temperatures. It has a characteristic odor; the cause of this is not known, as tin is not volatilized. It has a "cry" like cadmium. Its sp. gr., 7.29, is about the same as that of copper, and it is the most fusible of the common metals, having a melting point of 228°. Tin oxidizes very slowly in the air, and burns at a white heat. If tin be washed with dilute aqua regia, its crystalline structure can be readily seen. This appearance, like that seen in ice water tanks, is called "moirée métallique." It is dissolved by strong HCl, forming the chloride. Strong HNO_3 converts it into $H_{10}Sn_5O_{15}$, metastannic acid, which is insoluble. *Uses:* As salts of tin are not poisonous, tin is well adapted for cooking utensils; but as tin becomes brittle at high temperatures, and is expensive, sheet iron coated with tin is used. The surface of the iron is cleaned with acid and the plate put in a bath of melted grease. It is then put in melted tin, where it remains for a couple of hours, and is then transferred to a second bath of tin. It is next heated in a bath of melted grease, to let the excess of tin flow off and to anneal the tin plate. So in the inside we have a core of Fe, on the outside pure Sn, and between the two an alloy of Fe and Sn. Tin is also used for covering pins. The pins are put with tin into a solution of some substance that dissolves tin. The tin dissolves and is precipitated by the brass. Tin foil is made by beating out tin, but ordinary foil is Pb covered with tin. *Alloys.* Bronze is Cu and Sn. Britannia metal is Sb and Sn, or Sn, Sb, and brass. Pewter is Sn and Pb, or Sn and Sb. Solder is Pb and Sn; the coarser kind has more Pb than the finer. Sn with Hg forms the amalgam for silvering mirrors.

Tin forms two classes of compounds, the stannous SnO, $SnCl_2$, and the stannic, SnO_2, $SnCl_4$.

I. STANNOUS COMPOUNDS. STANNOUS CHLORIDE, $SnCl_2$, is formed by boiling Sn in an excess of HCl.

$$Sn + 2HCl = SnCl_2 + H_2.$$

It is white, crystalline, soluble, but its solution soon becomes turbid, owing to the formation of an oxychloride, insoluble, probably SnO_2H_2SnCl. It has a strong tendency to pass to $SnCl_4$, and therefore is a powerful reducer. If we add to a solution of $SnCl_2$ a solution of $HgCl_2$, a white precipitate of calomel is formed.

$$2HgCl_2 + SnCl_2 = SnCl_4 + Hg_2Cl_2.$$

Soon, however, if there is an excess of $SnCl_2$, gray metallic Hg is precipitated.

$$Hg_2Cl_2 + SnCl_2 = SnCl_4 + 2Hg.$$

$SnCl_2$ is used by dyers as a reducer, and also as a mordant, modifying the color of the dye. When a dunging agent, as Na_2CO_3, is added to it, stannous hydrate, SnO_2H_2, is precipitated.

$$Na_2CO_3 + SnCl_2 + H_2O = SnO_2H_2 + CO_2 + 2NaCl.$$

SnO_2H_2 is white. *Stannous Oxide*, SnO, is black. *Stannous sulphide*, SnS, is chocolate brown.

II. STANNIC COMPOUNDS. STANNIC CHLORIDE, $SnCl_4$, the most important of these, is a thin, colorless liquid. It is made by the action of Cl on Sn or $SnCl_2$. It is corrosive, and fumes in moist air. When mixed with one-third part of water, it solidifies to a soft mass called "butter of tin." A hydrated $SnCl_4$ obtained by dissolving Sn in aqua regia is much used in dyeing.

STANNIC ACID, H_2SnO_3, is made by adding NaOH to $SnCl_4$.

$$4NaOH + SnCl_4 = H_2SnO_3 + 4NaCl + H_2O.$$

Sn is in the same series as C, and therefore the hydrate has a form like H_2CO_3. It is an acid, because stannates can be formed from it. Some of these stannates, especially sodic stannate, are used as mordants, precipitating H_2SnO_3 in the fibre of the cloth. Upon treating Sn with HNO_3, a white substance is formed, which is not the nitrate, but which has apparently the same formula as stannic acid. It is, however, insoluble in most acids, while stannic acid is soluble in acids. From it we can get sodic metastannate, with a formula $Na_2H_8Sn_5O_{15}$. This metastannate must be derived, not from H_2SnO_3, but from an acid with a formula $H_{10}Sn_5O_{15}$. This acid therefore is called *metastannic acid.* We cannot distinguish between these acids by analysis; when heated they both yield SnO_2. *Stannic Oxide* or *Anhydride*, SnO_2, occurs native as tinstone. It is very hard, is used for enamels, and as putty powder to put the last polish on glass. *Stannic Sulphide*, SnS_2, is a dirty yellow, while SnS is a chocolate brown. SnS_2 dissolves in $(NH_4)_2S$, which is always formed in NH_4SH on standing. Ammonic sulphostannate is formed, probably $(NH_4)_2SnS_3$ corresponding to the stannates from stannic acid, with S in the place of O. There is a series of such salts from sulpho-stannic acid, H_2SnS_3, called sulpho-stannates. There is formed in NH_4SH on standing, besides $(NH_4)_2S$, some $(NH_4)_2S_2$. SnS dissolves in this, forming the same substance as above.

$$(NH_4)_2S_2 + SnS = (NH_4)_2S + SnS_2.$$
$$= (NH_4)_2SnS_3.$$

In either case, if an acid be added to the sulpho-stannate, SnS_2 is precipitated.

$$(NH_4)_2SnS_3 + 2HCl = 2NH_4Cl + H_2SnS_3.$$
$$= 2NH_4Cl + H_2S + SnS_2.$$

As CO_2 and SiO_2 are the annydrides of H_2CO_3 and H_2SiO_3, respectively, so SnS_2 may be regarded as a *quasi* anhydride, formed from sulpho-stannic acid by subtracting H_2S. Tin, antimony, and arsenic all form sulpho salts, thus furnishing a means of separating salts of Sn, Sb, and As, from salts of Pb, Bi, and kindred metals. SnS_2 is frequently prepared in a dry way by heating Sn, S, Hg, and NH_4Cl, forming brilliant gold colored scales called mosaic gold or bronze powder. The little scales are fastened on plaster casts to make them look like gold.

Bismuth, Bi, at. wt. 210, is one of the rarer of the common metals. It usually occurs native. It is produced chiefly in Saxony and England. The rock in which it occurs is put into a series of sloping tubes and heated. The Bi melts and runs down into dishes, while the rock is left behind. This process is called *liquation*, but has now been superseded. The appearance of Bi is characteristic; it is distinguished from all the other metals by a slight but distinct reddish tinge. It has a crystalline structure, breaks into crystalline plates, and has a low melting point, 262°. Its sp. gr. is about like most of the other common metals, 9.79. It is very brittle, and the pure metal has no uses. It is used to form *fusible alloy*, consisting either of Bi, Pb, and Sn, when it is called Rose's metal, and has a melting pt. of 93°; or of Bi, Cd, Sn, and Pb, when it is called Woods' metal, and has a melting pt. of 68°. Fusible alloy is used in stereotyping. A plaster cast is taken of the type, and melted fusible alloy poured in. The alloy expands on cooling and fills the cast. Fusible metal is used for safety plates in boilers. The higher the pressure of steam the greater the heat is. A plate of fusible alloy is put into the side of the boiler. The proportions of the metals in this plate are such that its fusing point is just below the point of extreme danger in the boiler. If, therefore, at any time the safety valve should refuse to work, the alloy will fuse out, and the steam will escape. Fusible alloy is also used in automatic fire extinguishers. Sprinklers are used, the holes of which are plugged up with fusible metal. When, therefore, the heat becomes great enough to melt the alloy, the water is let out.

Bismuth forms two classes of salts, the bismuthous, as Bi_2O_3, $BiCl_3$, and the bismuthic as Bi_2O_5. There are also a few compounds corresponding to the dioxide Bi_2O_2. *Bismuthous Nitrate*, $Bi(NO_3)_3$, the most important salt, is made by dissolving Bi in HNO_3. It is soluble in a small quantity of water, but when added to a large quantity of water it is precipitated as the basic or sub-nitrate, $BiNO_3(OH)_2$, which is like the hydrate, except that it has NO_2 in the place of one atom of H. This basic nitrate is one of the best remedies for dyspepsia. The forming of insoluble basic salts is characteristic of Bi. An oxychloride, BiOCl, called pearl powder, is formed by the action of water on $BiCl_3$. It is used to whiten the face. It is turned black by H_2S, since Bi_2S_3 is black.

Antimony. Sb, at. wt. 120, is more common than Bi. It has been known in the east for thousands of years, where its sulphide was used as a medicine, and by the Egyptian women to blacken their eyebrows. The metal was first obtained in the fifteenth century by Basil Valentine, a monk. The most important ore is stibnite, or antimony glance. It occurs in Hungary, Borneo, England, Canada, and the Hartz Mts. The Sb is separated from the gangue of its ore by liquation, and reduced like Pb by roasting in a reverberatory furnace, or by heating with iron. When heated with iron, the reaction is as follows:

$$2Sb_2S_3 + 6Fe = 6FeS + Sb_4.$$

Properties. Sb strongly resembles Bi in its qualities. It is crystalline, lustrous, volatile, burns readily in air, but is pure white. It has a sp. gr. of 6.7 and a mpt. of 425°. It does not rust in air at ordinary temperatures, and, like Sn, is converted by HNO_3 into a white powder. Sb stands next to Sn in Mendelejeff and there are many points of resemblance between them. The molecule of Sb probably has four atoms. The metal has no uses, but forms many important alloys. Type metal is an alloy of four parts lead to one part antimony. The Sb hardens the Pb and causes it to expand and fill the mould, while the Pb removes the brittleness of the Sb. Axle metal, an alloy of copper tin and antimony, or tin antimony and lead, is used to support the axles in machinery. It is hard enough to resist the pressure, but not hard enough to cut the axle.

Antimony forms two classes of compounds, the antimonious, Sb_2O_3, $SbCl_3$, and the antimonic, Sb_2O_5, $SbCl_5$. It also forms the oxide Sb_2O_4, which is made by fusing Sb and nitre.

I. ANTIMONIOUS COMPOUNDS. ANTIMONIOUS CHLORIDE, $SbCl_3$, is formed by dissolving stibnite in HCl.

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

It is a white, crystalline, soft mass, whence its common name "butter of antimony." It is volatile and corrosive. Like BiCl it dissolves in a little H_2O, but is precipitated by a large amount, forming an oxychloride, SbOCl, of a white color, called "algaroth powder" by the alchemists. All the other antimonious salts, except tartar emetic, are precipitated by water, forming basic salts. Gun barrels are bronzed by rubbing them with $SbCl_3$. *Antimonious Iodide*, SbI_3, has three modifications. The difference here, as probably in HgI_2, is merely one of molecular weight. The green modification is SbI_3, and the red Sb_3I_9, but the composition of the brown is unknown.

ANTIMONIOUS SULPHIDE, Sb_2S_3, is formed by adding H_2S to a soluble antimonious salt.

$$2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl.$$

This reaction takes place when the substances are cool, while in the reaction for making $SbCl_3$, the substances are heated. Sb_2S_3 occurs in nature as stibnite, gray and crystalline, but when made in the wet way it is orange red and non-crystalline, or amorphous. If the red variety is heated, it turns black and fuses, forming the gray sulphide. HgS, on the contrary, when crystalline, is red; when amorphous, black. The chief uses of the red modification of Sb_2S_3 are as a pigment under the name of antimonious vermillion, and in vulcanizing rubber. The black modification is used in making fireworks, and in matches. Sb_2S_3, like SnS_2, is soluble in $(NH_4)_2S$, forming probably $(NH_4)_3SbS_3$, ammonic sulphantimonite. From this the sulphide is precipitated by the addition of an acid.

$$2(NH_4)_3SbS_3 + 6HCl = 6NH_4Cl + 3H_2S + Sb_2S_3.$$

Tartar Emetic, $SbOKC_4H_4O_6H_2O$, is a double tartrate of K and Sb, formed by replacing H_2 in tartaric acid, $H_2C_4H_4O_6$, by K and the univalent radical SbO ($-Sb=O$). It is a valuable medicine, and alone of all soluble antimonious salts is not decomposed by H_2O. Sb forms a hydride, SbH_3, antimonetted hydrogen, a colorless inflammable gas.

II. ANTIMONIC COMPOUNDS. *Antimonic Oxide* or *Anhydride*, Sb_2O_5, is yellowish white. The only salt of any importance derived from the acid corresponding to this anhydride, is *Potassic Pyroantimoniate*, $K_2H_2Sb_2O_7$. This is a salt of pyroantimonic acid, $H_4Sb_2O_7$, which is formed by the decomposition of $SbCl_5$ in H_2O. A corresponding Na salt can be obtained which is the only insoluble simple sodic salt. It is, therefore, sometimes used to separate sodic from potassic salts in analysis. Metantimonic acid, $HSbO_3$ is formed by dissolving Sb in HNO_3. It is a white powder, insoluble in H_2O, and forms a series of salts called metantimoniates. *Naples Yellow* is a basic lead metantimoniate. *Antimonic Chloride*, $SbCl_5$, is a liquid. *Antimonic Sulphide*, Sb_2S_5, is orange yellow; it is the anhydride of a sulpho-acid corresponding to pyroantimonic acid. Sulphantimoniates occur native.

Arsenic, As, at. wt. 75, is rather more abundant than Sb. It has been known for a long time, and is obtained in Silesia from *Mispickel*, an isomorphous mixture of FeS_2 and $FeAs_2$ in varying proportions. In the centre of the arsenic regions in Silesia As is so abundant that it has permeated to the well-water and has given it a distinct taste. Silesia produces about one-half of all the As produced, but large quantities are obtained in England by roasting tin ore. Considerable As is got at Freiburg in Saxony from *Smaltine*, an ore of Co and Ni. As is also found native. *Extraction*. The ore is roasted in muffles with holes to let the air pass through. If the ore is mispickel, the As and S burn, and the volatile As_2O_3 and SO_2 are carried up through tall chimneys called poison towers, by a draft so powerful that none of the arsenic can escape. The arsenic condenses in the towers, and falls in a white powder called poison meal. This poison meal must be removed from the towers, and if impure, resublimed. It is a very dangerous operation to remove the As_2O_3 from the towers, and the workmen are obliged to be encased in leather with wet cloths over their mouths and nostrils. The resubliming is done in iron kettles. A number of drums are attached to the kettle one above another, the joints of which are made tight by clay. Most of the As_2O_3 condenses on the sides of the drums, forming a thick, transparent, glassy crust called vitreous arsenic; but part of it goes off as vapor and is collected by poison towers.

ARSENIOUS ANHYDRIDE, As_4O_6, should be called *white arsenic* but it is usually called simply arsenic. It has two modifications. The symbol of arsenious anhydride is proved by the vapor density to be As_4O_6 instead of As_2O_3. When kept in air the vitreous variety, which is amorphous, becomes crystalline, passing to the opaque variety. In commerce both the pulverulent and the vitreous forms of As_4O_6 are used. Both forms have a slight sweetish taste, are white, odorless, almost insoluble in water, more soluble in HCl, volatile and poisonous. *Uses:* As_4O_6 is used as poison, for killing rats and sometimes for murders and suicides. It is bad for murders and suicides, however, since death is slow and painful, and the least trace can be detected with the utmost certainty, even when the body has been buried a long time. In Styria and Tyrol the inhabitants eat arsenic as a regular habit; it is said to improve the wind and make the women fairer. In taking arsenic it is necessary to begin with a small quantity, and the dose can be increased so that enough can finally be taken to kill a beginner at once. After the habit of arsenic eating has been acquired it must be left off gradually; otherwise the arsenic eater would be poisoned just as if he had taken a large dose for the first time. The antidote is ferric hydrate, a solution of which is sold by druggists under the name of "dialyzed iron." It forms with the arsenic an insoluble compound. White arsenic is used in preserving animal matter from decomposition, in anatomy to coagulate the blood, in making shot, and as a source of other As compounds.

POTASSIC ARSENITE, K_3AsO_3. The acid of the anhydride As_4O_6 would be H_3AsO_3, but it is unknown, being too unstable to exist.

Corresponding to it, however, there are salts called Arsenites. The potassic arsenite is white and soluble, and is used in medicine under the name of Fowler's solution. It is a powerful alterative. *Argentic Arsenite*, Ag_3O_3As, egg yellow, is sometimes used as a test for As. *Cupric Arsenite* is green and insoluble, and is used as a pigment under the name of "Scheele's green"; its formula is unknown. Mixed with cupric acetate it forms Schweinfurth green, often called Paris, or emerald green. Paris green is very poisonous; it is very brilliant, and is used as a pigment in many ways. Dresses are often dyed with it, but it comes off easily; in fact the green is often fastened on with starch. It is also used to color leaves in artificial flowers, in paper for wrapping candy, in children's paint boxes, and in much green paper. But the most dangerous use is in paper hangings. Olive green and even brown paper is apt to have arsenic. The danger is that the coloring matter rubs off, and the arsenic forms with organic matter arsenetted hydrogen, a very poisonous gas.

ARSENIC, As_4, is made by heating arsenious anhydride with charcoal.

$$As_4O_6 + 3C = 3CO + As_4.$$

As_4 is silver white, on the border line between the metals and the non-metals, and is a poor conductor of electricity. It is crystalline, brittle, and tarnishes on exposure to air; this may take place rapidly enough for the As to take fire. It readily volatilizes, giving a characteristic garlic odor, which forms a valuable rough test. But the best test is the formation of AsH_3.

ARSENETTED HYDROGEN, AsH_3. As and N stand in the same series of Mendelejeff's table, and As forms a hydride AsH_3, which is a gas, corresponding to NH_3. It is formed by the action of nascent H on any compound of As. It is one of the most dangerous substances known; a single bubble is enough to produce sickness and a horrible death. Gehlen, a German chemist, experimenting with AsH_3, died in nine days from smelling the joints of his apparatus. AsH_3 is very combustible, and this fact is made the basis of Marsh's test for As. The compound containing As is converted by nascent H to AsH_3. This is then burned, and a cold porcelain dish pressed down upon the flame. Metallic arsenic is deposited on the porcelain, making a glossy black stain called "arsenic mirror." This mirror is soluble in NaOCl. SbH_3 acts in the same way as AsH_3, but the Sb mirror formed is not soluble in NaOCl. Another form of Marsh's test is to pass the AsH_3 through a glass tube previously heated to redness. The gas is decomposed and an As mirror formed on the sides of the tube.

ARSENIC ANHYDRIDE, As_2O_5 is made by oxidizing As_4O_6 with HNO_3. It forms transparent glassy masses, which, after deliquescing, when heated to 100°, first melt and then yield H_3AsO_4 as a crystalline precipitate. It is readily reduced to As_4O_6 or to the metallic state, and hence is used to furnish O in preparing the aniline dyes. Enormous amounts are used for this purpose. Rosaniline is green with a metallic lustre. When dissolved in alcohol it gives a magenta solution. A great number of purple and green dyes are obtained from this magenta dye. As_2O_5 corresponds to H_3AsO_4, arsenic acid. *Argentic Arseniate*, Ag_3AsO_4, is made as follows:

$$Na_3AsO_4 + 3AgNO_3 = Ag_3AsO_4 + 3NaNO_3.$$

It has a reddish color whereas argentic arsenite is yellow.

SULPHIDES. The sulphide As_2S_2 occurs in nature as the mineral *Realgar*. It is often called Sandarach. It can be made artificially by fusing As_4O_6 and S. There is no corresponding oxide. It is used as a pigment and in white fire. The sulphide As_2S_3 occurs in nature as the mineral *Orpiment*, yellow. It is formed whenever H_2S is added to arsenious anhydride.

$$As_4O_6 + 6H_2S = 2As_2S_3 + 6H_2O.$$

It is used as a pigment, called "king's yellow," prepared by subliming As_4O_6 and S. It is used as a depilatory. It dissolves in $(NH_4)_2S$, forming a sulpho-acid, probably $(NH_4)_2As_2S_4$. As_2S_5 is formed from arsenic acid by H_2S. $AsCl_3$ is a volatile, colorless, oily liquid. In contact with a little water it forms an oxychloride, viscid and semitransparent.

Phosphorus, P, at. wt. 31. This element is widely distributed, but is not often found in large quantities in the mineral kingdom. It is distributed through the soil as phosphates, chiefly phosphates of calcium and iron. *Vivianite* is a phosphate of iron. *Apatite*, $Ca_5F(PO_4)_3$, is probably the substance that occurs in the soil and makes it fertile by dissolving in rain and fluids; it is then taken up by the plants. If the P in the soil is exhausted, the field is allowed to lie fallow and the apatite is gradually dissolved. Natural manure, which contains calcic phosphate, is the proper thing to restore P to the soil. Animals get calcic phosphate from the vegetables they eat. The artificial manures commonly used are bone ash, calcic phosphate, or other phosphates. Bones consist largely of calcic phosphate. Guano is partly fossilized bird excrement containing calcic phosphate. Phosphorus was discovered in 1669 by Brand, in urine, and Kunkel subsequently described the product thus obtained. It was then considered a chemical curiosity. But P was not made in any great quantity till Scheele and Gahn in the last century discovered that it could be made from bone ash. When P first began to be used on a large scale for matches, the price fell from 75 cts. an ounce to 75 cts. a pound. *Extraction.* Phosphorus is got chiefly from bone ash. The bones are burned till the gelatine passes off, leaving calcic phosphate, $Ca_3(PO_4)_2$. This ash is treated with H_2SO_4, forming calcic superphosphate, or acid calcic phosphate.

$$Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4.$$

The gypsum is precipitated, and the solution of $CaH_4(PO_4)_2$ is evaporated to dryness, and then heated till it loses two molecules of H_2O, becoming calcic metaphosphate.

$$CaH_4(PO_4)_2 = Ca(PO_3)_2 + 2H_2O.$$

The object of the above processes is to get a phosphate with less Ca than there is in bone ash. The metaphosphate is then heated in an earthen retort with carbon.

$$3Ca(PO_3)_2 + 10C = P_4 + 10CO + Ca_3(PO_4)_2.$$

The method by which P is prepared can be used on a very large scale. The P distills over and is collected in copper receivers filled with water. The P is then passed through wash leather and cast into sticks. For this purpose it is melted in hot water in tanks, and flows out through glass tubes into cold water. In 1873 about 1200 tons of phosphorus were produced, requiring 15,000 tons of bones.

ORDINARY PHOSPHORUS, P_4, when first prepared is colorless and transparent, but soon becomes covered with a grayish white coating caused by the P splitting off and H_2O getting under the surface. P has a peculiar odor and resembles wax; at ordinary temperatures it is soft and pliable, but at very low temperatures it is brittle and hard. The fusing point of P is 43°; consequently it melts in warm water. Its boiling point is 290°, and its most striking property is its inflammability. If a draft of air be introduced upon the P when under warm water, the P takes fire, giving off a thick white smoke, and leaving behind a reddish substance supposed to be a suboxide. P combines with the air at ordinary temperatures, giving off a faint light called phosphorescence, from which the element gets its name. P therefore has to be kept under water or alcohol. Phosphoresence is usually due to a slow combustion, but not always; for phosphorescence is emitted by phosphorus even when placed in gases which have no oxygen. P has a very low sp. gr., 1.83. It is insoluble in water and alcohol, slightly soluble in ether, very soluble in carbonic disulphide. Its solution is very inflammable, and it has been proposed to use it in warfare as "Modern Greek Fire." The vapor of P is poisonous and produces caries of the jaw. *Uses:* The most important use is in making matches. Matches are made of wood, S, P, and oxidizing agents. The red tip of a match is a sort of gum paste, mixed with P and the oxidizers, which are minium or black oxide of manganese, and KNO_3. The P takes fire at a much lower temperature than usual, in the O given up by these agents. The P ignites the S, and this in turn kindles the wood. P is also used in making the aniline dyes. (See under the chlorides.) P is very useful in medicine to restore phosphates; it is also used to kill rats.

RED OR AMORPHOUS PHOSPHORUS. P exists in several forms. When a substance occurs in several different modifications, each possessing different physical and chemical properties, these modifications are called *allotropic forms*. P exists thus in several forms, but red P is the only one well established, except ordinary P. It was discovered by Schrötter in 1856. It is prepared by heating P for a long time at a temperature of 240°, in an atmosphere essentially of N in a closed iron vessel. The brown crust thus formed is treated with CS_2 to remove all traces of ordinary P. Red P is almost the exact opposite of ordinary P in its properties. The latter is crystalline, while the former is non-crystalline, or *amorphous*. It is not inflammable, but at 260° it is converted to ordinary P, which takes fire. It is, moreover, neither poisonous nor volatile, is insoluble in CS_2, infusible, not phosphorescent, and has no odor. The cause of the difference between the two modifications is probably the difference in the number of atoms in the molecule, but the vapor density of red P cannot be determined, as on heating it is changed to the common variety. *Uses:* It is used in safety matches, which can be lighted only on the box. On the tip of the matches there is a mixture of inflammable Sb_2S_3 and oxidizing agents, $KClO_3$, $K_2Cr_2O_7$, and minium. On the box there is glue, umber, MnO_2, Sb_2S_3, and red P. The umber is an earthy oxide of Fe put on to prevent the box from taking fire. Although red P will not ignite when scratched under ordinary conditions, yet it will ignite with $KClO_3$. When the match is drawn over the box, it ignites the P on the box, and thus kindles the match. The advantages of safety matches are that there is less danger of fire and of poisoning, but they are inconvenient to use. Sometimes a mixture of red P and $KClO_3$ is used in the manufacture of ordinary matches.

Phosphoretted Hydrogen, PH_3, may be made by treating P with NaOH and H_2O.

$$P_4 + 3NaOH + 3H_2O = PH_3 + 3NaPO_2H_2.$$

Another way is to decompose calcic phosphide, Ca_3P_2, in H_2O.

$$Ca_3P_2 + 6H_2O = 2PH_3 + 3CaO_2H_2.$$

PH_3 is an inflammable gas, and has a strong smell like that of decayed fish. It is apparently spontaneously inflammable; this spontaneous combustion, however, is due, not to PH_3, but to the liquid P_2H_4, an impurity. It has been supposed from its inflammability that will-o'-the-wisps were PH_3; but PH_3 has never been found native, and will-o'-the-wisps are probably some hydrocarbon. PH_3 resembles NH_3, and we should expect to get salts of phosphonium, PH_4, like those of ammonium, NH_4. The only one of these, however, that we can obtain is PH_4I, and this is very unstable.

P forms many acid hydrates; H_3PO_2, hypophosphorous acid, H_3PO_3, phosphorous acid, H_3PO_4, orthophosphoric acid, HPO_3, metaphosphoric acid, and $H_4P_2O_7$, pyrophosphoric acid. In the two phosphorous acids P is trivalent. Corresponding to phosphorous and phosphoric acids, respectively, are the anhydrides P_2O_3 and P_2O_5. P_2O_4 is the anhydride of a recently discovered acid.

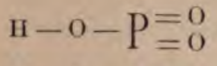
PHOSPHORIC ANHYDRIDE, P_2O_5, is the white smoke formed by burning P in the air.

$$P_4 + 5O_2 = 2P_2O_5.$$

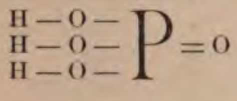
It is a white powder, looking like snow. It has an extremely strong attraction for water, and hisses in it like red hot iron. It is used as a dehydrater in organic chemistry.

THE PHOSPHORIC ACIDS. These can be formed by treating P_2O_5 with water, or dissolving P in HNO_3 and evaporating. *Orthophosphoric* or *Phosphoric Acid*, a thick syrup, is first obtained; by partially evaporating this syrup the *Pyrophosphoric Acid*, $H_4P_2O_7$, is obtained, and by evaporating to dryness *Metaphosphoric Acid*, HPO_3, a glassy substance often called glacial acid. In all these acids P is quinquivalent, and we can suppose them all derived from the normal hydrate, PO_5H_5, by subtracting water.

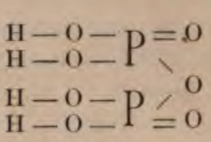
$PO_5H_5 - H_2O = H_3PO_4$, orthophosphoric.
$2H_3PO_4 - H_2O = H_4P_2O_7$, pyrophosphoric.
$H_3PO_4 - H_2O = HPO_3$, metaphosphoric.
$2HPO_3 - H_2O = P_2O_5$, phosphoric anhydride.



$$H-O-P\begin{array}{l}=O\\=O\end{array}$$



$$\begin{array}{l}H-O-\\H-O-\\H-O-\end{array}P=O$$



$$\begin{array}{l}H-O-\\H-O-\end{array}P\begin{array}{l}=O\\ \diagdown\end{array}\\ \qquad\qquad\quad O\\ \begin{array}{l}H-O-\\H-O-\end{array}P\begin{array}{l}\diagup\\=O\end{array}$$

These acids are not important in themselves, but the salts derived from them are important.

ORTHOPHOSPHATES OR PHOSPHATES. These are derived from H_3PO_4. Each atom of H in this acid can be replaced by a radical, and we can therefore get three phosphates, if the radical be univalent. Thus from Na we have NaH_2PO_4, Na_2HPO_4, and Na_3PO_4.

The *disodic phosphate*, Na_2HPO_4, is the most important, and is prepared from calcic superphosphate by the action of Na_2CO_3.

$$CaH_4(PO_4)_2 + 2Na_2CO_3 = 2Na_2HPO_4 + CaCO_3 + H_2O + CO_2.$$

It crystallizes with $12H_2O$, in large rhomb-shaped crystals, and is the salt usually meant by sodic phosphate. It is the source of the other phosphates. On being heated it loses water and forms sodic pyrophosphate, $Na_4P_2O_7$. To get the argentic orthophosphate, Na_2HPO_4 is treated with an excess of $AgNO_3$.

$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3.$$

Argentic phosphate is light yellow. The neutral calcic phosphate, insoluble, is formed by adding a soluble calcic salt to the disodic phosphate.

$$3CaCl_2 + 2Na_2HPO_4 = Ca_3(PO_4)_2 + 4NaCl + 2HCl.$$

Acid magnesic phosphate is formed by adding $MgSO_4$ to disodic phosphate.

$$MgSO_4 + Na_2HPO_4 = MgHPO_4 + Na_2SO_4.$$

$MgHPO_4$ is partially soluble in water, and the difference in solubility between the calcic and magnesic salts is accounted for by the fact that the calcic is a neutral while the magnesic is an acid salt. If, therefore, the H in the magnesic salt be replaced by NH_4, we get a less soluble salt. The formation of this ammonium salt is a good way of precipitating Mg.

$$MgHPO_4 + NH_4OH = MgNH_4PO_4 + H_2O.$$

Upon heating, this is broken up into $Mg_2P_2O_7$, H_2O, and NH_3. *Calcic superphosphate*, $CaH_4(PO_4)_2$, is the best of the artificial manures. It is also used as a yeast powder, and as a medicine in nervous disease, restoring P to the brain. *Microcosmic salt*, $NaNH_4HPO_4$, is made by adding an ammonic salt to the disodic phosphate.

$$Na_2HPO_4 + NH_4Cl = NaNH_4HPO_4 + NaCl.$$

Microcosmic salt is used in blowpipe analysis.

METAPHOSPHATES. Sodic Metaphosphate, $NaPO_3$, can be got by heating microcosmic salt, or, like all the other metaphosphates, by heating the dihydrogen orthophosphate.

$$NaNH_4HPO_4 = NaPO_3 + H_2O + NH_3.$$

$$NaH_2PO_4 = NaPO_3 + H_2O.$$

PYROPHOSPHATES. These are formed by heating the monohydrogen orthophosphate, *e. g.*,

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

Magnesic pyrophosphate can also be obtained by heating $MgNH_4PO_4$.

CHLORIDES. Phosphorus Trichloride, PCl_3, and Phosphorus Pentachloride, PCl_5, are formed by passing Cl over P. PCl_3 is a liquid, PCl_5 a solid, light yellow. Their most important property is their behavior when treated with water. PCl_3 forms the phosphorous acid.

$$PCl_3 + 3H_2O = PO_3H_3 + 3HCl.$$

PCl_5 is decomposed by water, forming an oxychloride, a thick brown liquid.

$$PCl_5 + H_2O = PCl_3O + 2HCl.$$

This action with water leads to an important use in organic chemistry, since any substance derived from water has the same action with these chlorides as water itself has; *e. g.* acetic acid, HOC_2H_3O.

$$PCl_3 + 3HOC_2H_3O = PO_3H_3 + 3C_2H_3OCl.$$

Methyl alcohol, CH_3OH, is another example.

$$PCl_3 + 3CH_3OH = PO_3H_3 + 3CH_3Cl.$$

Phosphorous iodide acts in the same way as PCl_3, forming with methyl alcohol CH_3I, methyl iodide. Methyl iodide is important, converting rosaniline to purple and violet dyes. On treating rosaniline with CH_3I, a part of its H is replaced by the univalent radical methyl, setting free HI. The color formed varies from purple to blue, according to the amount of H replaced by methyl. *Phosphorous Bromide*, PBr_3, is a transparent liquid, which acts like PCl_3.

Silicon, Si, at. wt. 28, next to O is the most abundant of the elements. O constitutes about one half the earth, and Si about one half the rest. It does not occur native, but is a constituent of all important rocks except limestones and dolomites. The metal silicon was discovered in 1823 by Berzelius. It is obtained from potassic fluo-silicate, K_2SiF_6, by heating with sodium.

$$K_2SiF_6 + 2Na_2 = Si + 2KF + 4NaF.$$

Like C, which stands directly over it in Mendelejeff, Si occurs in three modifications. (1) Obtained as above it is a brown powder, and resembles charcoal. (2) When dissolved in melted aluminum, it separates out in reddish crystals like diamond. (3) When intensely heated in a closed vessel, the brown powder becomes compact and infusible, and of a form resembling graphite. By burning Si, SiO_2 is formed.

SILICETTED HYDROGEN, SiH_4, is formed by treating Mg_2Si with HCl.

$$Mg_2Si + 4HCl = 2MgCl_2 + SiH_4.$$

This is a gas, spontaneously inflammable. As we go along the third row of Mendelejeff the stability of the hydrides increases; thus SiH_4 is spontaneously inflammable, PH_3 is readily inflammable, H_2S moderately inflammable, and HCl incombustible.

SILICIC ANHYDRIDE, SiO_2, occurs in nature as quartz, which is crystalline, and is the most abundant of all minerals. It has no cleavage, but has a conchoidal fracture. Quartz occurs pure in large transparent crystals called rock crystals. Amethyst is a purple rock crystal. Chalcedony is a translucent quartz, and has two varieties, called carnelian and bloodstone. Jasper is an opaque variety of quartz, colored red by ferric oxide. A mixture of quartzes of various degrees of transparency constitutes agate. Onyx is an agate with parallel bands. Sand is powdered quartz; sandstone is merely sand cemented together. SiO_2 occurs in a different species as *Opal*, sometimes colored. The play of colors in opal, called opalescence, is due to minute cracks which cause the light to be variously reflected. SiO_2 is taken up from the soil by plants and stored in their tissues, especially in their stalks. The stiffness of bamboo, wheat, and grass, is due to SiO_2. Equisetum, or mare's tail, contains so much that it can be used for polishing purposes. Diatoms are species of microscopic plants. The plant dies, and the shells consisting of SiO_2 are left behind in great quantities. This forms a good material for polishing, since it is very fine. This powder is sometimes known as tripoli, since large deposits are found in Tripoli. SiO_2 is found in the animal kingdom only in the feathers of some birds. It can be artificially prepared by adding an acid to a soluble salt of Si.

$$Na_2SiO_3 + 2HCl = 2NaCl + H_2SiO_3.$$

H_2SiO_3 is rather unstable, and upon heating breaks up into SiO_2 and H_2O. SiO_2 is insoluble, except in hydrofluoric acid and the alkalies. It is hard, will scratch glass, and is used for polishing it. When made in this way it is a fine, white powder, very light.

SILICIC ACIDS. By adding HCl to Na_2SiO_3, as above, we obtain a gelatinous precipitate, which is at first probably H_4SiO_4. This loses water in the air, passing through various degrees of hydration, like the phosphoric acids. The most important of these silicic acids is H_2SiO_3, a hard jelly-like mass; but many silicates from the other silicic acids are known, as serpentine, $Mg_3Si_2O_7$, from $H_6Si_2O_7(2H_4SiO_4 - H_2O)$. On heating the acid to 100° the H_2O is all expelled, and SiO_2 is left. Chalcedony was probably once a jelly, but lost H_2O, becoming SiO_2. Some petrified wood was formed in a similar way.

SILICATES. Since each atom of H in the silicic acids may be replaced by an atom of a univalent radical, we can get a great many complex silicates. Felspar and mica, constituents of granite, are chiefly silicates of aluminum. Clay is a silicate of Al and Fe. Hornblende is essentially a silicate of Mg. Silicates occur in nearly all earths. Glass and pottery are artificial silicates. *Water glass*, or *Soluble glass*, is a sodic or potassic silicate, formed by heating sodic or potassic carbonate with sand, *e. g.*

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2.$$

Silicic acid is a weaker acid than carbonic acid at ordinary temperatures. But it is a general principle depending on Berthollet's law that at high temperatures a weaker acid will drive out a stronger one, if the stronger acid is volatile and the weaker nonvolatile. Therefore in the reaction above SiO_2 will replace CO_2. Water glass, as made, is usually colored by impurities. It is slightly efflorescent, and dissolves slowly in hot H_2O, being the only silicate soluble in H_2O. Water glass is used as a cement under the name of Egyptian Tenexine, and in fresco painting to prepare the walls for the fresco. Another important use is in making artificial stone, and in preserving stone which has begun to crumble. The House of Parliament in England had begun to crumble, but it was washed with water glass, and has lasted well ever since.

GLASS. Glass was known very early: it is found in Egyptian tombs, colored green or blue from impurities. In classic days glass was good and well worked. Roman glass, by being buried in the earth, has scaled off and shows iridescent colors. At the fall of the Roman Empire the art of glass-making was forgotten in Europe, but survived in the East, and was brought to Venice. At one time the business of glass-making died out in Venice, but it has lately been revived. The art was carried to Bohemia, and the glass made there has been famous ever since. From Bohemia the art spread. Glass is a mixture of an alkaline silicate and some other silicate. Alkaline glass has the advantages of being destitute of a crystalline structure, and of passing through a viscous state in cooling; but it is not hard enough for ordinary purposes, is soluble, fusible, and efflorescent. Calcic silicate on the other hand is hard, insoluble, and not efflorescent; but it is crystalline, and does not pass through the viscous state. A mixture, however, of water glass and calcic silicate combines the advantages of both without their disadvantages. There are two varieties of glass, depending on the silicates mixed with water glass.

I. CROWN GLASS is a silicate of Ca with sodic or potassic silicate. (*a*) *Bohemian Glass* is a silicate of Ca and K. It is hard and very slightly fusible, usually of a slight greenish color, and is used almost exclusively for chemical ware that has to stand great heat. It is very expensive. (*b*) *Window Glass*, a mixture of sodic and calcic silicates, is the material of all ordinary chemical ware, windows, etc. It is made from sodic carbonate, sand, and calcic hydrate; some broken glass, or cullet, is put in, to make the mass combine more easily. In the Bohemian glass K_2CO_3 is used instead of Na_2CO_3. The materials are put into chambers heated by the waste heat of the fire, and "fritted," or roasted, but not fused, driving off the CO_2 and H_2O. They are then transferred to small pots where they fuse, forming melted glass. The glass is now ready to be worked. This is ordinarily done by blowing it. In the *Crown Process* a long iron tube called a blow pipe is inserted into the pot, and a lump of glass taken out on the end. By blowing through the tube and at the same time twirling it, this lump is expanded into a sort of flask. Then a second workman fits a heated iron rod called a "pontil" on the side of the flask opposite the blow pipe, which is then cut out. The pontil serves merely as a handle. The glass is then carried to the "glory hole," which is a hole in the side of a furnace, where the heat is intense. The pontil is rested on a support, and revolved; the great heat makes the glass viscous, and the centrifugal force flattens it out. The plate is cut up into panes; the central pane has the mark of the pontil, and is sold for cellar windows. This process of shaping the glass is called the crown process, and from it the whole variety of crown glass received its name. In the *Cylinder Process*, as in the crown process, the glass is blown into a pear-shaped flask. This is then swung by a man standing on a bridge till the glass assumes the shape of a cylinder with rounded ends. The cylinder is rolled on an inclined plane, and then opened and flattened by wood into a plate. It is then ready for annealing. During the process the glass must be occasionally heated at the glory hole. *Plate Process*. The glass made by the crown and cylinder processes is liable to be thicker in some places than in others, and cannot be made into very large panes. By the plate process plates can be made of uniform thickness. The melted glass is poured on an iron table with edges raised according to the thickness desired. The glass is then rolled, and can be made either plane, fluted, or designed, according to the roller used. The plate is next smoothed by rubbing together two plates with sand and water between. The glass after this has an opaque appearance, making ground glass. It is polished with emery, and lastly with rouge, Fe_2O_3, or putty powder, SnO_2. (*c*) *Bottle glass* is a silicate of Ca and Na containing Fe and Al. It is usually green, due to ferrous silicate, but sometimes brown from ferric silicate. It is used for ordinary bottles, and no pains are taken to get the materials pure. It is made in the same general way as ordinary window glass.

II. FLINT GLASS. This is always a silicate of Pb and K, since Na would give it a color. It is more fusible than crown glass.

and more lustrous, but is softer and does not resist chemical agents so well. (*a*) *The common variety* is used for table ware, as tumblers, decanters, etc. The materials used for making it are minium, litharge, sand, pearlash, nitre, and cullet; they must be free from all impurities which would color the glass. The materials are first fritted as in crown glass, and then fused. The fusing is done in arched dome-shaped pots with openings at the sides. The pot is nearly air tight and opens into the outer air away from the fire of the furnace. These precautions are taken to prevent the hydrocarbon gases of the furnace from reducing the oxide in the glass to metallic lead, thus blackening the glass. As a still further precaution, minium, and nitre are used in the glass to furnish oxygen. A lump of glass is removed as before, and blown or moulded. The finest specimens, as wine glasses, are done by blowing. A ball of glass is blown, on the bottom of which is placed an elongated lump of glass, forming the stem. At the end of the stem is fastened another globe of blown glass, which is cut in two and spread out, forming the bottom. The cup is formed by cutting off the top of the upper globe, and widening out the bell. For ordinary tumblers and goblets two moulds are used, one for the outside, and the other for the inside. A lump of glass is put into the outer mould, and the inner mould is pressed down upon it. For bottles a lump of glass is put into an iron mould, and spread over its inner surface by blowing. The glass ware is heated and polished with a stick. If the ware were now allowed to cool suddenly, the outside would cool quicker and be stretched over the inside, so that the glass would be in a state of tension, and would be shattered by a slight blow. It must, therefore, be annealed. Annealing is a slow cooling. The ware is passed slowly through "leers" or long ovens heated only at one end. In passing from the heated to the cool end, the glass is cooled slowly and uniformly. The process takes twenty-four hours. So-called "tough glass" is glass annealed in a bath of oil. The common ware, usually called pressed glass, is now ready for use, but the finer varieties are usually cut. Cutting is done by pressing the ware against a rapidly revolving wooden wheel fed with sand and water. It is then polished, first by emery and lastly by rouge. Engraving is a finer process of cutting, done by small copper wheels fed with emery and water. In etching the design, the surface of the glass is covered with wax or varnish, and the design cut through the wax. Hydrofluoric acid is poured on, which eats away the glass and leaves the design. The sand blast is a recently invented method for making ground glass. The glass plate is exposed to a blast of air or steam charged with sand. By covering parts of the glass even with very delicate articles, as lace, a perfect design of the covering is formed. Colored glass is glass colored by some oxide. Ruby glass is colored by purple-of-Cassius. But colored glass is expensive, and hence glass is often flashed. Flashed glass is glass colored only on the outside, and is made by dipping white glass taken from the retort into melted colored glass. With flashed glass, designs in different colors can thus be easily got. Since the base and the outside layer are of different colors the outside coat has merely to be ground off. (*b*) *Paste* is a flint glass containing a large amount of plumbic silicate. It is used in imitating diamonds and the precious stones. (*c*) *Optical glass* contains much plumbic silicate. It is used in making lenses. The object aimed at is to get glass of a uniform density. For this purpose the glass is melted in crucibles and stirred with an earthenware rod. When the glass cools, it arranges itself according to its density, the denser parts at the bottom; consequently, when the glass is cut into horizontal sections, plates can be got of nearly the same density throughout. One reason of the high cost of large lenses is the difficulty of getting thick layers of uniform density. (*d*) *Enamel* is merely flint glass made opaque by some white powder which is infusible at the temperature at which glass melts. The usual enamel powders are stannic oxide and bone ash, but Sb_2O_3 and As_2O_3 are sometimes used.

Silicic Chloride, $SiCl_4$, is a colorless volatile liquid, converted by H_2O into H_2SiO_3 and HCl. It is made from SiO_2 by heating a mixture of SiO_2 and carbon in a stream of chlorine.

$$SiO_2 + 2C + 2Cl_2 = 2CO + SiCl_4.$$

This is a concurrent reaction.

Boron, B, at. wt. 11, is one of the rarer common elements. It occurs in the form of *Borax*, $Na_2B_4O_7$, and in some springs as *Boric Acid*, H_3O_3B. Borax is found in Thibet, California, and Ceylon. Most of the boron of Europe is obtained from boric acid, which occurs in the Tuscan maremma in lagoni or pools, and also suspended in the volcanic jets of steam which issue from the ground, called fumarolles or suffioni. Basins are built over the suffioni and filled with water from the neighboring springs, thus forming artificial lagoni. As the steam jets pass up through these lagoni the soluble boric acid is absorbed by the water. When the lagoni are charged with H_3O_3B the solution is drawn off into settling tanks and evaporated by the heat of the spring. Boric acid thus obtained is in the form of large pearly crystalline scales, feeling like spermaceti, and not volatile. Boric acid may also be made from borax by H_2SO_4 and water.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O = 4H_3O_3B + Na_2SO_4 .$$

The hydrate can act either as an acid or as a base. Another name for boric acid is Sassoline. *Boric anhydride*, B_2O_3, is white. The borates of the alkaline metals are freely soluble, those of the other metals sparingly soluble in H_2O, freely soluble in HNO_3. None are entirely insoluble.

Borax, $Na_2B_4O_7$, called also sodic tetraborate, can be made from boric acid; if $5H_2O$ be subtracted from $3H_3O_3B$ we get the acid corresponding to borax, $H_2B_4O_7$. When heated. borax first swells up and loses its water of crystallization, and then fuses to a colorless glass; this glass has the power of dissolving metallic oxides, and hence it forms a valuable blowpipe test. When fused with oxide of cobalt the glass has a blue color with oxide of chromium, green. The use of borax in soldering is to dissolve oxides formed on the surfaces of the metals when heated, which prevent them from uniting with the solder. The fusible borax glass formed is squeezed out between the metallic surfaces. The use of borax as a flux depends on the same principle as in soldering. It is used as a glaze, in making enamels, in dyeing, and as a medicine. It is used in washing as a substitute for soap. The test for boric acid and borax is a brown color with turmeric paper even in acid solutions. A mixture of alcohol and boric acid burns with a greenish flame. We can get this flame with any borate by adding alcohol, and H_2SO_4 to set free the H_3O_3B.

Boric chloride BCl_3, is a colorless volatile liquid. The element boron can be obtained from potassic fluoborate by heating it with Na or K.

$$KBF_4 + 3K = 4KF + B.$$

Boron has two modifications, corresponding to the diamond and charcoal modifications of carbon. The crystalline modification is said to be harder than diamonds.

Fluorine, F, at. wt. 19. The element is more common than boron. Its name is derived from *Fluor Spar*, CaF_2, an important source. This was formerly used as a flux; hence its name from *fluere*, to flow. Fluor spar has many different colors, of which purple, green, and yellow are the most common. When pure it is white. Fluor spar has the property of changing the color of the light which passes through it. This property is called fluorescence and is possessed by some other substances, as uranium and organic compounds. It crystallizes in cubes or octahedra. An important source of fluorine is *Cryolite* or sodic fluoaluminate, $Na_6F_{12}Al_2$, which occurs in Greenland and is largely exported. Fluorine is a constituent of bones but only in small amounts. The element F is the only one of the thoroughly studied elements that has never been obtained. It cannot be isolated since fluorine is so corrosive that no vessel will hold it. The nearest approach is a vessel of CaF_2.

HYDROFLUORIC ACID, HF, is obtained from cryolite or fluor spar by the action of H_2SO_4. The process is usually done in platinum retorts.

$$H_2SO_4 + CaF_2 = CaSO_4 + 2HF.$$

HF is a gas. fumes in air from the absorption of water, is very soluble in water and very corrosive, attacking any silicate; hence it cannot be kept in glass. The bottles used are usually of gutta percha or metal. It acts also on organic matter and its vapor is extremely poisonous. It was used in etching glass even before 1670. Scheele in 1671 first determined its formula. and in 1810 it was thoroughly studied by Gay Lussac and Thenard. Smooth etching is done by using HF in a liquid state, rough etching by using the vapor. Engravings were formerly made by etching on glass ; done in this way they were better than steel engravings. This process is called hyalography.

SILICIC FLUORIDE, SiF_4, is made by dissolving SiO_2 in HF.

$$SiO_2 + 4HF = Si\ F_4 + 2H_2O.$$

SiF_4 is a colorless gas, and when it is passed through H_2O, every bubble becomes covered with a white jelly-like substance H_2SiO_3, and the solution has an acid reaction. The substance formed is H_2SiF_6, called fluosilicic acid.

$$2SiF_4 + 3H_2O = H_2SiO_3 + H_2SiF_6 + 2HF.$$

As we have sulpho-acids in which S takes the place of O in ordinary acids, so here we have an acid in which two atoms of F take the place of each atom of O in H_2SiO_3. Fluorine and oxygen stand next each other in Mendelejeff's table. SiF_4 is a *quasi* anhydride from H_2SiF_6, corresponding to SiO_2, the anhydride of H_2SiO_3. H_2SiF_6 is a liquid, and is got in the above reaction by filtering ; it forms several important fluosilicates. K_2SiF_6 is nearly insoluble, while Na_2SiF_6 is soluble. This gives a means of separating sodic from potassic salts. This fact is interesting, for K_2PtCl_6 is insoluble, while Na_2PtCl_6 is soluble. Ba and Sr can also be separated in the same way, since $BaSiF_6$ is insoluble while $SrSiF_6$ is soluble. *Boric fluoride*, BF_3, a gas, when passed through water gives fluoboric acid, HBF_4. This acid corresponds to HBO_2, derived from H_3O_3B by subtracting H_2O.

Chlorine, Cl, at. wt. 35.5. This element is very abundant in the form of NaCl.

CHLORINE, Cl_2, was discovered by Scheele towards the end of the 18th century ; but HCl and NaCl were known before. It is prepared by heating black oxide of manganese with HCl.

$$4HCl + MnO_2 = MnCl_4 + 2H_2O.$$
$$= MnCl_2 + 2H_2O + Cl_2.$$

$MnCl_4$ is very unstable, easily breaking up to $MnCl_2$ and Cl_2. Cl_2 is a greenish yellow gas, heavier than air ; its sp. gr. referred to hydrogen gas is 35.5, while that of air is about 15. Cl_2 is therefore collected by downward displacement. It cannot be collected over H_2O since it is soluble, forming chlorine water, which has a yellowish green color and gives off chlorine at ordinary temperatures. Chlorine has a strong pungent odor, and is very corrosive and poisonous. It attacks the lungs, rendering them especially liable to a sudden chill followed by pneumonia. The best antidote is the vapor of ether inhaled. By passing Cl_2 through water at about the freezing point, a definite compound of chlorine and water is obtained, with a formula $Cl5H_2O$, called hydrate of chlorine. This freezes in yellowish green crystals, which are very unstable. By pressure or freezing, chlorine, like most soluble gases, can be condensed into a liquid. If crystals of $Cl5H_2O$ be put in one end of a bent tube sealed at both ends, and gently heated, they break up into chlorine and water. The pressure increases, and as the chlorine cannot escape it is condensed at the other end of the tube, as an oily liquid. If a jar of chlorine and free hydrogen be exposed to the sunlight, or if a mixture of the two be touched with a lighted match, the chlorine and hydrogen combine with a violent explosion, forming HCl. When exposed to diffused light the chlorine and hydrogen combine slowly. Cl has a very strong attraction for H as seen by this and the following experiments: (1) If Cl water be exposed to light, bubbles rise which are found to be O, while the liquid left is shown to contain HCl.

$$2H_2O + 2Cl_2 = 4HCl + O_2.$$

This experiment takes two or three days, but if the Cl water be in contact with some substance that combines readily with O, the action is more rapid. If a piece of wet calico print be put into Cl gas it is at once bleached, while dry calico is not affected. The reaction is the same as that above, except that the O, instead of being set free, oxidizes, or burns up, the coloring matter. This is a good example of a concurrent reaction. (2) Coal gas is a mixture of hydrocarbons, but is essentially CH_4. If a mixture of chlorine and coal gas be lighted, HCl is formed, and a large amount of C is set free in the form of soot. (3) If Cl water be added to H_2S, HCl is formed, and S is precipitated.

$$H_2S + Cl_2 = 2HCl + S.$$

Chlorine also has a strong attraction for metals. If tinsel, leaves of brass, be put in a jar from which the air is exhausted, and the mouth of this jar connected with another jar filled with Cl_2, the Cl_2 rushes in upon the tinsel, which burns brilliantly, forming $ZnCl_2$ and $CuCl_2$. If powdered antimony be dropped into a jar of Cl_2, it burns like tinsel. Cl combines with all the elements except perhaps F.

HYDROCHLORIC ACID, HCl, is the muriatic acid of commerce. It is usually made by the action of H_2SO_4 on NaCl in Le Blanc's process [p. 12]. It is a colorless gas, soluble in water, the solution usually yellow from impurities, either Fe_2Cl_6, or some organic compound. HCl is heavier than air (sp. gr. 18.25 referred to H) and fumes in moist air from the absorption of water. It is condensible, has a strong, pungent smell and an acid reaction. Of the chlorides AgCl, Hg_2Cl_2, and Cu_2Cl_2 are insoluble in water. $PbCl_2$ is slightly soluble in cold, freely soluble in hot water. All the rest are soluble.

COMPOUNDS OF CHLORINE AND OXYGEN. The most important of these are,

Cl_2O	HOCl	hypochlorous anhydride and acid.
Cl_2O_3	$KClO_2$	chlorous anhydride and potassic chlorite.
ClO_2	———	chloric dioxide.
(Cl_2O_5)	$HClO_3$	chloric acid.
(Cl_2O_7)	$HClO_4$	perchloric acid.

Cl_2O_5 and Cl_2O_7 do not exist. Cl_2O is a yellowish green gas, very explosive, since Cl and O have weak affinities for each other. It is prepared by passing Cl_2 over mercuric oxide.

$$HgO + 2Cl_2 = Cl_2O + HgCl_2.$$

When dissolved in water it forms HOCl, which readily parts with its O, and hence is a powerful bleaching agent. From HOCl are formed the *hypochlorites*.

CHLORIDE OF LIME, or BLEACHING POWDER, $CaOCl_2$, is made by treating moist slaked lime with Cl_2, which is gradually absorbed.

$$CaO_2H_2 + Cl_2 = CaOCl_2 + H_2O.$$

The best way of writing the graphical formula is Cl—O—Ca—Cl. The theory that the substance is a mixture of $CaCl_2$ and CaO_2Cl_2 is untenable; one reason being that, if it were, it would be deliquescent, since $CaCl_2$ is deliquescent. When in solution, however,

$CaOCl_2$ is decomposed, and $CaCl_2$ and CaO_2Cl_2 are formed. If an acid be added, as HCl, or H_2SO_4, Cl_2 is given off.

$$2H_2SO_4 + CaO_2Cl_2 + CaCl_2 = 2CaSO_4 + 2HOCl + 2HCl.$$
$$= 2CaSO_4 + 2H_2O + 2Cl_2.$$

This property leads to important uses of chloride of lime as a bleaching agent and as a disinfectant. Chloride of lime is the material with which cotton and linen are bleached. Cl gas could be used, but it is inconvenient, as it escapes. The bleaching powder sets free just as much Cl_2 as is wanted, and no more. The cloth is first dipped into a solution of bleaching powder, and then into dilute H_2SO_4. The Cl_2 set free combines with the H in the water of solution, while the O is attracted by the dye. Bleaching depends upon the fact that the dye is more combustible than the cloth; animal fibres, such as wool and silk, cannot be bleached in this way, since they would be attacked by the O sooner than the dye. Bleaching necessarily weakens the cloth, since the O does combine with it to some extent. The cloth must be carefully washed, since any Cl_2 or H_2SO_4 left in it would rot the fibre. Chloride of lime is used as a disinfectant. Pieces of cloth dipped in a solution of $CaOCl_2$ are hung up in the room to be disinfected. The CO_2 present in the air acts as the acid, setting free Cl_2. This sets free O from the water on the cloth, and the O burns up the offensive organic matter. *Chlorous anhydride*, Cl_2O_3, is a yellowish green gas, very explosive. In moist air it is gradually transformed into $HClO_2$, from which a number of unstable salts called *chlorites* may be formed.

POTASSIC CHLORATE, $KClO_3$. By boiling bleaching powder, or better by passing Cl_2 into boiling milk of lime, we get $Ca(ClO_3)_2$.

$$6CaO_2H_2 + 6Cl_2 = Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O.$$
$$6CaOCl_2 = 5CaCl_2 + 5O + CaOCl_2.$$
$$= Ca(ClO_3)_2 + 5CaCl_2.$$

The calcic chlorate is treated with KCl, forming $KClO_3$.

$$Ca(ClO_3)_2 + 2KCl = CaCl_2 + 2KClO_3.$$

$CaCl_2$ is very soluble in cold water, while $KClO_3$ is not very soluble. Therefore they can be separated by crystallization, the $KClO_3$ crystallizing out in characteristic flat plates, white, with a pearly lustre. The only important property of $KClO_3$ is its instability.

$$2KClO_3 = 2KCl + 3O_2.$$

This is the usual way of making O. If MnO_2 be added, the O is given off at a lower temperature. When $KClO_3$ is heated with a combustible substance, the O is given off more readily. If $KClO_3$ and S be ground together in a mortar, they combine with little explosions, forming SO_2. When mixed with P, $KClO_3$ explodes with a slight blow. For these reasons $KClO_3$ is used as an oxidizer in fireworks, matches, and blasting powder. In blasting, the S and $KClO_3$ must be mixed on the spot, owing to the ease with which they explode when mixed. If HCl be added to $KClO_3$, Cl_2 and one of its oxides are given off. If H_2SO_4 be used instead of HCl, $HClO_3$ is formed, but like H_2CO_3 under similar conditions it immediately breaks up into water, ClO_2, and O.

$$4KClO_3 + 2H_2SO_4 = 2K_2SO_4 + 2H_2O + 4ClO_2 + O_2.$$

ClO_2 is an unstable gas, very explosive. If the mixture of H_2SO_4 and $KClO_3$ be heated in a test tube, each bubble of ClO_2 explodes as it is formed. Consequently, if sugar be mixed with $KClO_3$, and a drop of H_2SO_4 be added, ClO_2 is formed, which at once explodes, giving off heat enough to set the sugar on fire in the O of the $KClO_3$. Potassic chlorate is cooling, and is used for throat diseases. $HClO_3$ is a liquid, very unstable.

POTASSIC PERCHLORATE, $KClO_4$, is obtained by heating $KClO_3$. If the reaction be stopped at the right stage we have

$$4KClO_3 = KCl + 3O + 3KClO_3.$$
$$= KCl + 3KClO_4.$$

It crystallizes in octahedra, and is one of the least soluble K salts. *Perchloric Acid*, $HClO_4$, is the most stable of the compounds of Cl and O, though when in contact with organic matter, as paper, it explodes violently. It is a liquid, but combines with water to form a solid hydrate.

Chlorine forms with ammonia a chloride of nitrogen, the formula of which is uncertain. It is a yellow oily liquid, and is the most explosive substance known, exploding when touched with a feather. Chloroform, $CHCl_3$, is made from $CaOCl_2$ and alcohol and smells like rotten apples. It is more dangerous than ether.

Bromine, Br, at. wt. 80, was discovered in 1826 by Balard in bittern. Br was formerly obtained exclusively from bittern, but two important sources have recently been discovered. The salt springs of Ohio, especially near Pomeroy, contain chiefly bromides, and Br is exported to Europe from these springs. The second source is the Abraum salts of Stassfurth. After the Mg and K salts have been extracted, the waste is treated for Br, and consequently this can be sold very cheap. America now produces more than half the Br in use in the world. The method of extraction of Br is similar to that of Cl. At Stassfurth the action takes place in stone tanks, and the gas is condensed in earthen coolers.

$$2H_2SO_4 + MnO_2 + 2KBr = K_2SO_4 + MnSO_4 + 2H_2O + Br_2.$$

The salt from which it is usually obtained, however, is $MgBr_2$. As there is almost always some Cl_2 present, the Br_2 must be purified by redistillation over KBr. The Cl_2 decomposes the KBr, forming KCl and setting free Br_2. Bromine is a reddish liquid, the only liquid element except mercury. It gets its name from Βρῶμος, a stench. It smells like Cl_2, but is stronger and more corrosive. It acts on the lungs, and one drop on the hand makes a painful sore. At — 7.3° it freezes into a gray substance looking like iron. It is slightly volatile at ordinary temperatures, boils at 63°, giving off a brownish red vapor. It is a little more soluble than Cl_2, and its solution is called bromine water. In the presence of a combustible substance Br, like Cl, combines with the H of H_2O, forming HBr and giving off O. Therefore Br can be used as a bleacher, acting however more slowly than Cl. Since the large supply of Br was discovered, it has been proposed to use it instead of Cl in bleaching. Br is closely related to Cl, and acts in substantially the same way. If Br vapor is brought in contact with H_2S, S is precipitated, and HBr is formed.

$$H_2S + Br_2 = 2HBr + S.$$

With coal gas Br acts like Cl. Hot Sb dropped into Br takes fire, and a white substance, $SbBr_3$, is formed. Br has rather weaker attractions for metals than Cl. With water at about the freezing point Br forms a hydrate, $Br5H_2O$, similar to the hydrate of Cl. On the oxidizing properties of Br depends its action in converting CoO_2H_2 to $Co_2O_6H_6$ [reaction p. 77].

HYDROBROMIC ACID, HBr, is like HCl in nearly all its properties, but is more unstable. Therefore HBr cannot be made like HCl, since the air and H_2SO_4 would decompose it. It is usually made by treating Br with H_2S according to the reaction above. To get the pure acid, bromide of phosphorus is treated with H_2O.

$$PBr_3 + 3H_2O = 3HBr + PO_3H_3 .$$

HBr has recently been discovered to be an antidote for quinine poison. The bromides resemble the chlorides. They are mostly white; AgBr however is slightly yellow. AgBr and Hg_2Br_2 are the only bromides which are entirely insoluble in water, though several others are only sparingly soluble. *Potassic Bromide*, KBr, is made from ferric bromide and potassic carbonate. It is white, soluble, and used as a medicine in cases of epilepsy, delirium tremens, and nervous diseases. It is the only opiate that produces sleep without danger. AgBr is used in photography. While Br has a weaker attraction for metals than Cl has, it has a stronger attraction for O. *Potassic bromate*, $KBrO_3$, occurs, but is not of much importance.

Test for bromides. The presence of Br can be detected by adding Cl to the solution. Br is set free, which colors the solution red. *e. g.*

$$2KBr + Cl_2 = 2KCl + Br_2 .$$

If the amount of Br is too small to color the whole liquid, CS_2 or ether may be added, dissolving the Br. If CS_2 be used, it sinks to the bottom, if ether be used it rises to the top; in either case taking with it the Br. Thus the Br, being confined to a small space, can be easily seen.

Iodine, I, at wt. 127, is widely but sparingly distributed. It was discovered in 1811 by Courtois. It occurs in mineral springs and also in sea water, but in such small quantities that it does not pay to extract it. Seaweeds, however, take up I into their tissue, and this can be extracted by burning the plants. These seaweeds are found chiefly in Scotland, Jutland, and Normandy, and kelp is the most important. While Br costs about seventy cents a pound, I costs from three to five dollars a pound. The reason of this difference is that I is used in the aniline dyes for making methyl iodide, and kelp and varec, the only important sources of I, cannot be obtained in sufficient quantities. I is extracted like Br. After the ash is treated to obtain the iodide, heat is applied, and MnO_2 and H_2SO_4 are added.

$$2KI + MnO_2 + 2H_2SO_4 = K_2SO_4 + MnSO_4 + 2H_2O + I_2.$$

The I distils over, collecting in pear-shaped receivers fitting one into another. I is a gray, crystalline solid with a metallic lustre; it is not a metal, however, for it combines with metals to form well defined salts. It has an odor like sponge, and these contain a small amount of I. It is very volatile at ordinary temperatures, having a violet vapor [ιώδης, violet], which is heavier than the vapor of any other element. Its mpt. is 107°, bpt. 180°. It is slightly poisonous and corrosive, slightly soluble in water, very soluble in alcohol and CS_2. The alcohol solution of iodine, called tincture of iodine, is used in medicine. In chemical action I resembles Cl and Br, but acts less readily upon H and metals; it decomposes H_2S, but not H_2O.

$$H_2S + I_2 = 2HI + S.$$

It unites directly with Sb, forming SbI_3, red, but there is no flame produced. Since I has not an attraction for H strong enough to decompose water, it cannot be used as a bleaching agent.

Hydriodic Acid, HI, is made in the same ways as HBr. *e. g.*

$$PI_3 + 3H_2O = PO_3H_3 + 3HI.$$

Its properties are like those of HBr, except that is less stable. *Iodides.* These are many of them colored, but some are colorless, as NaI and KI. AgI is used in photography. NaI is less stable than KI, and gradually decomposes. PbI_2 is yellow. PI_3 is used in preparing the aniline dyes. The only iodides entirely insoluble in water are AgI, Hg_2I_2, HgI_2, and BiI_3. *Iodides of Nitrogen* are formed by adding ammonia to tincture of I. This gives a black powder, a mixture of the various iodides, the most important of which are NI_3 and NI_2H. They are nearly all as explosive as the chlorides of N. *Iodic acid*, HIO_3, is a solid, rather stable, and from it is formed *potassic iodate*, KIO_3. I_2O_5 is an anhydride from this acid.

Test for Iodine and Iodides. If a drop of starch paste be added to the colorless tincture of I, the liquid is changed to a deep indigo color. The iodides have no action with starch paste, but when Cl_2 is added, I is set free, which colors the paste. This is a very delicate test; one part of I in five hundred thousand parts of H_2O can easily be detected, and some claim that the test is even finer than this.

The last three elements which we have treated, Cl, Br, and I, constitute the *chlorine group*. These elements come under each other in Mendelejeff's great periods, and the properties vary as we go down the series, thus:

	State.	Color.	Attr. for H and metals.	Attr. for O.
Cl	Gas	Yellow	Much	Weak
Br	Liquid	Reddish brown	Less	More
I	Solid	Violet or gray	Less	More

They are all corrosive, all have pungent odors, all are soluble in water, all decompose H_2S. This is a strong point of Mendelejeff's table.

Sulphur, S, at. wt. 32, is one of the most common of the elements after the first ten. It occurs in nature both as native sulphur and in combination, as sulphates and sulphides. (1) Most of the sulphur of commerce is obtained from native sulphur in the volcanic regions, chiefly those of Sicily and of Tuscany in Italy. Small quantities are also obtained from Iceland, where the supply is almost inexhaustible. (2) Sulphur is obtained from the decomposition of gypsum. (3) Small quantities are also got by roasting various sulphides, chiefly Cu_2S. *Extraction.* In Sicily sulphur is obtained from deep mines, called Solfara. The sulphur is generally associated with a white volcanic earth, and is usually visible, sometimes in large crystals. In Sicily the sulphur earth is heaped up in piles on brickwork, and covered with earth. These piles are called *calcarone.* The sulphur is then lighted, and about one-third of it escapes as SO_2 through a chimney in the top, while the rest melts and flows off through holes in the bottom. The piles are about 30 ft. across and 7 ft. deep, and the process takes from thirty to ninety days. Although this process is very wasteful, most of the sulphur used is obtained from it. In Italy the earth is found chiefly in the crater of an extinct volcano near Puzzuoli. This crater, the floor of which consists of sulphur, is called Solfatara. The sulphur earth is usually placed in iron or earthen retorts, which are packed in a furnace. The sulphur distills over into jars placed outside the furnace, where it condenses to a liquid. The liquid S flows out at the bottom of these jars into a pail and solidifies. If the earth is very rich in S, it can be simply heated in caldrons, and the sulphur ladled out. Sulphur obtained in these ways is very impure, and is known as "crude sulphur." It must therefore be purified, or refined. Much of the refining is done at Marseilles. The crude sulphur is placed in caldrons and moderately heated. It is volatilized, and the gas passes slowly into a cold chamber, where it at once condenses and falls in a crystalline powder, called "flowers of sulphur." At a higher heat, the sulphur volatilizes and passes over so quickly that it heats the brick walls, and hence condenses to a liquid. It is then cast into sticks in wooden moulds, and receives the name of "roll brimstone." A very finely divided form of sulphur, called "milk of sulphur," is obtained chemically; it is prepared by adding an acid to a disulphide.

$$K_2S_2 + 2HCl = 2KCl + H_2S + S.$$

The more finely divided sulphur is, the whiter it appears. Roll brimstone is yellow, flowers of sulphur lighter, and milk of sulphur nearly white. *Uses:* Sulphur is used in medicine, matches, gunpowder, in making ultramarine and the compounds of sulphur, and in vineyards to kill the phylloxera.

ALLOTROPIC FORMS. (1) *Rhombic.* This is the ordinary form of sulphur and it occurs crystalline in nature, usually in large yellow octahedra; these crystals can be got artificially by dissolving S in CS_2 and allowing the solution to evaporate. The rhombic form is very brittle, has a shiny lustre like glass, and a sp. gr. of 2.05. (2) *Prismatic.* This form is got by heating S to a moderate heat, and then letting it cool. It crystallizes in long needle shaped prisms, is of a deeper yellow than the rhombic, has a waxy lustre, and a sp. gr. of 1.98. It is unstable, readily passing to the rhombic form. Although in this case the needle-like shape is retained, yet these needles when pulverized break up into little rhombs. (3) *Viscous.* This form is made by melting sulphur, and pouring it when hot into cold water. It has the consistency of soft molasses candy, and passes to the rhombic form even more readily than the prismatic variety. Its color is very dark yellow, and its chief use is in taking casts. It is pressed against the model when soft, and in a short time hardens, being changed to the rhombic form. *Properties:* S is insoluble in almost all liquids except CS_2. It melts at 114°, becoming a yellow liquid which flows easily. When the temperature is carried higher, the liquid turns dark reddish, and becomes so viscous that the containing vessel can be turned upside down. If the temperature is carried still higher, to the boiling point, 440°, it again becomes liquid. S is very combustible, and is distinguished by the disagreeable smell of its compounds, *e. g.* SO_2, H_2S, CS_2.

SULPHURETTED HYDROGEN, H_2S, the most important of the compounds of S and H, occurs in nature in many volcanic exhalations, in small quantities in the atmosphere, and in the water of many springs, where it is formed by the decomposition of organic matter containing S, and by the action of organic matter on gypsum or any other soluble sulphate. In the laboratory it is usually made by the action of an acid on ferrous sulphide.

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

The H_2S made in this way is not pure, as FeS usually contains some uncombined Fe, which generates H when treated with H_2SO_4. To get pure H_2S, antimonious sulphide is dissolved in HCl.

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

H_2S is a colorless gas, smells like rotten eggs, is soluble in water, and has a sp. gr. of 17. It can be condensed to a liquid, as we should expect of a soluble gas, has a slight acid reaction, is poisonous except when largely diluted with air, and combustible, giving a blue flame from the SO_2 formed.

$$H_2S + 3O = H_2O + SO_2.$$

If there is a free supply of air, this reaction takes place; if there is not enough air, the following:

$$2H_2S + O_2 = 2H_2O + S_2.$$

A similar effect is produced if an oxidizer, as HNO_3, is added to H_2S in solution. In this case S is precipitated, and the red fumes of either NO_2 or N_2O_3 are given off. H_2S, therefore, is a strong reducing agent. Charcoal has a very large surface and consequently possesses in a high degree the property of condensing gases. If powdered charcoal be put into a jar of H_2S, and when saturated with it, be plunged into a jar of O, the H_2S will burst into a flame and burn in the O. For the action of Cl on H_2S see Chlorine.

SULPHIDES. H_2S forms many salts, called sulphides. Of these the sulphides of the alkaline metals (NH_4, Na, K, etc.) and those of the alkaline earths (Ca, Mg, Sr, Ba) are soluble in water; all the rest are insoluble. The division of the elements into groups in qualitative analysis is based on the solubility of the sulphides. For example, if to a solution containing the nitrates of all the basic radicals, H_2S be added, all sulphides insoluble in acids will be precipitated. Since the sulphides of As, Sn, and Sb, are soluble in $(NH_4)_2S$, they can be dissolved out by treating the precipitated sulphides with $(NH_4)_2S$. Thus we separate sulphides soluble in water and acids, sulphides soluble in $(NH_4)_2S$, insoluble in water, and sulphides insoluble in water, acids, and $(NH_4)_2S$. *Potassic Sulphydrate*, KSH, an acid salt of H_2S, is formed by the action of H_2S on KOH.

$$KOH + H_2S = KSH + H_2O.$$

If an excess of KOH be added, neutral *potassic sulphide* is formed.

$$KSH + KOH = K_2S + H_2O.$$

The above is a typical method of making the alkaline sulphydrates and sulphides; but a better way of making the soluble sulphides is to heat the sulphate with charcoal.

$$K_2SO_4 + 2C = K_2S + 2CO_2.$$

Potassic sulphide in solution has a strong alkaline reaction. The insoluble sulphides are prepared in various ways. The common method is to treat a salt of the element, usually a soluble salt, with H_2S, $(NH_4)_2S$, or NH_4SH.

$$FeCl_2 + (NH_4)_2S = FeS + 2NH_4Cl.$$

$$CuCl_2 + H_2S = CuS + 2HCl.$$

If the sulphide formed by H_2S is soluble in acids, it can be precipitated by neutralizing the free acid with NH_4OH. It is not always necessary that the salt treated should be soluble, *e. g.*

$$PbO + H_2S = PbS + H_2O.$$

The reaction of H_2S on $Pb(C_2H_3O_2)_2$, precipitating PbS, black, is used as a test for H_2S. The sulphides of the heavy metals are often prepared by heating the metal with S.

$$Fe + S = FeS. \qquad 2Cu + S = Cu_2S.$$

In some cases they can be obtained by the action of H_2S on the metal.

$$Ag_2 + H_2S = Ag_2S + H_2.$$

Hydric Persulphides. There are many compounds of S and H, called the hydric persulphides, as H_2S_2, H_2S_3, H_2S_4, H_2S_5. They are corrosive, very unstable, and are heavy oily liquids, smelling like H_2S. They are all acids, and have corresponding salts called persulphides. These persulphides are made by boiling or fusing the hydrates with an excess of S. Then upon adding HCl, if the conditions are right, the corresponding acid will be obtained; otherwise it will break up into H_2S and S.

$$K_2S_2 + 2HCl = 2KCl + H_2S + S.$$

All the persulphides are yellow. Liver of sulphur, chiefly K_2S_5 but very impure, is formed by fusing K_2CO_3 and S.

Sulphuric Anhydride, SO_2, occurs in nature in volcanoes, sometimes in large quantities, as would be expected, since it is the product of S burned in air.

$$S_2 + 2O_2 = 2SO_2$$

S burns with a pale blue flame. The most common way of preparing SO_2 is by dissolving Cu in H_2SO_4.

$$Cu + 2H_2SO_4 = CuSO_4 + H_2 + H_2SO_4.$$
$$= CuSO_4 + 2H_2O + SO_2.$$

The nascent H in the first reaction acts on the H_2SO_4, forming H_2SO_3, which breaks up into H_2O and SO_2. Another way of preparing SO_2 is by heating C and H_2SO_4. This way, of course, is more economical than the other, but the SO_2 given off is mixed with CO_2.

$$2H_2SO_4 + C = CO_2 + 2H_2O + 2SO_2.$$

Properties: SO_2 is a colorless choking gas, with an acid reaction, rather more soluble in water than CO_2, poisonous, and producing all the effects of an ordinary cold. It is one of the most easily condensible of all soluble gases; at —8° it becomes a colorless liquid; and at —76°, a solid. It does not support combustion, and hence is used for extinguishing burning chimneys. The solution of SO_2 in water, H_2SO_3, is called *sulphurous acid*. This solution is like H_2CO_3, the solution of CO_2 in water. The properties of H_2SO_3 and H_2CO_3 are similar: H_2SO_3 is a stronger acid than H_2CO_3 but neither of them can exist free; the sulphites, like all the carbonates except the alkaline carbonates, are insoluble or nearly so; if an acid be added to either, there is an effervescence and CO_2 or SO_2, as the case may be, is given off. But there is one marked difference between the sulphites and the carbonates: the sulphites readily take up O, passing to the sulphates, while the carbonates cannot take up O. The same is true of the corresponding acids. *Uses:* SO_2 is used as a bleacher. It does not, like Cl_2, burn up the color, but combines with it to form a colorless compound. For this reason SO_2 is used to bleach substances that are too delicate to stand chlorine, especially animal fibres, as wool, silk, etc. Straw, also, has to be bleached by SO_2, as Cl_2 would color it yellow. With chlorine there is no way to restore the color; but if the SO_2 be driven off, either by adding a stronger acid or by neutralizing the SO_2 with an alkali, the color returns. Thus white flannel often turns yellow when washed with soap, and the sun and acids in the air turn straw hats yellow. SO_2 is used in skin diseases; it is useful in cases of animal and vegetable parasites. Since sulphites and sulphurous acid absorb O, they are powerful reducing agents. By means of them the permanganates are converted, first to the manganates, and then to the manganous salts, while the sulphurous acid is oxidized in the process to sulphuric acid. Similarly if HNO_3 be added to H_2SO_3 or SO_2, the red fumes of NO_2 are given off, and H_2SO_4 is formed. This experiment illustrates the method by which H_2SO_4 is manufactured.

SULPHURIC ACID, H_2SO_4. The manufacture of H_2SO_4 is the most important of all chemical processes, since so many substances are obtained from H_2SO_4. Nearly every important chemical process except metallurgy depends directly or indirectly on H_2SO_4. The essence of the process consists in oxidizing SO_2 to H_2SO_4 by HNO_3, as above, and in reconverting the nitrous fumes given off to HNO_3. The SO_2 is formed in America by burning sulphur, and in England, where most of the H_2SO_4 is made, by dropping FeS_2 on red hot triangular bars of iron. The HNO_3 is usually got by the action of H_2SO_4 on $NaNO_3$. SO_2, HNO_3, air, and steam pass up into a large chamber lined with sheet lead, containing water in the bottom. Here this reaction takes place:

$$SO_2 + 2HNO_3 = H_2SO_4 + 2NO_2. \qquad (1)$$

The H_2SO_4 formed is dissolved in the water in the chamber. Since HNO_3 is itself made from H_2SO_4, and to get two molecules of HNO_3 it is necessary to use one molecule of H_2SO_4, only as much H_2SO_4 is made in the reaction above as is used up in the manufacture of the HNO_3. But the NO_2 formed unites with the steam, forming more HNO_3, which can act on a fresh portion of SO_2.

$$4NO_2 + H_2O = 2HNO_3 + N_2O_3. \qquad (2)$$

The N_2O_3 formed in (2) also unites with H_2O forming HNO_3.

$$3N_2O_3 + H_2O = 2HNO_3 + 4NO. \qquad (3)$$

Nitrous oxide absorbs O from the air to form NO_2.

$$2NO + O_2 = 2NO_2. \qquad (4)$$

The process now begins over again at reaction (2); thus the HNO_3 serves merely as a carrier to bring H and O to the SO_2. Thus with a very little HNO_3 an indefinite amount of H_2SO_4 can be made. In practice, however, it is found better to let the nitrous fumes pass off after they have used up all the air that enters the chambers with the SO_2. The fumes are conducted into towers lined with sheet lead, known as Gay Lussac's towers. These towers are filled with brick or coke, over which strong H_2SO_4 trickles, dissolving the fumes, and flowing out at the bottom. This H_2SO_4 is then reintroduced into the chamber, and becomes diluted by the water at the bottom, giving up the nitrous fumes, which then unite with steam and air to form HNO_3, according to reactions (2), (3), and (4); thus the process is continuous. The dilute acid which collects at the bottom of the chambers is known as "chamber acid," and must be concentrated. A cheap method of concentrating the acid is by the use of Glover's towers. These are towers packed with coke, like Gay Lussac's towers; but they are placed between the furnace and the chamber. The chamber acid trickles over the coke, and is concentrated by passing through it the hot current of SO_2 on its way to the chamber. Since acid concentrated in Gay Lussac's towers is apt to take up organic impurities, to get a purer H_2SO_4 some other method must be used. The acid is usually concentrated by evaporating in lead pans till it becomes strong enough to attack the lead; it is then drawn off by siphons into platinum or glass stills, and the water distilled off. Since glass is apt to break, platinum, though very expensive, is cheaper in the long run. *Properties:* H_2SO_4 is an oily liquid, white when perfectly pure, but in commerce usually yellow. It is heavier than water, sp. gr. 1.83, and boils at 310°. The acid is a poor conductor of heat, and if a lamp be held underneath, the lower part is heated to the boiling point, and bubbles rise. When they meet the cold H_2SO_4, they are condensed, and the liquid falls back with a shock; this is called "bumping." Consequently when H_2SO_4 is heated in a glass vessel, the vessel is liable to break unless it be heated all around. H_2SO_4 has a great attraction for H_2O, and, when combining with it, gives off enough heat to boil ether; it is therefore a powerful drying agent. Since it has so strong an attraction for water, H_2SO_4 will remove H_2O from those substances which contain H and O in the proportions to form H_2O. Thus if sugar, $C_{12}H_{22}O_{11}$, is mixed with a little H_2SO_4, the H_2SO_4 combines violently with the H and O of the sugar, leaving it a mass of charcoal. H_2SO_4 removes the H_2O from wood and most organic substances, leaving them charred. For this reason it is very corrosive on the skin. *Impurities:* The usual impurities in H_2SO_4 are $PbSO_4$ from the lead pans, H_2O absorbed from the air, nitrous fumes absorbed in the manufacture, arsenic, and, when Glover's towers are used, $Fe_2(SO_4)_3$. $PbSO_4$ is soluble in strong hot H_2SO_4, slightly soluble in cold, and insoluble in weak H_2SO_4. Chemically pure H_2SO_4 may be obtained by distillation of the acid itself. *Uses:* H_2SO_4 is used in the manufacture of Na_2CO_3 and K_2CO_3 by Le Blanc's process, in the preparation of certain artificial manures, in the manufacture of alizarine, in dyeing, and in making nitroglycerine, ether, chloroform, and almost all the important acids and chemical substances. Thus we see how exceedingly important are the uses of H_2SO_4. *Sulphates.* H_2SO_4, being dibasic, forms both neutral and acid salts, *e. g.* K_2SO_4 and $KHSO_4$. The only insoluble sulphates are $BaSO_4$, $SrSO_4$, $PbSO_4$; $CaSO_4$ is only slightly soluble. $BaSO_4$ is also insoluble in HCl, and its formation is used as a test for sulphuric acid and the sulphates. The group of vitriols and the group of alums are sulphates.

NORDHAUSEN OR FUMING SULPHURIC ACID, $H_2S_2O_7$. In the lead chamber process H_2SO_4 is used in the manufacture of H_2SO_4; hence H_2SO_4 must originally have been made in some other way. The acid used was the Nordhausen acid. It is made by distilling $Fe_2(SO_4)_3$, or green vitriol, $FeSO_4$, in earthenware flasks, and it was therefore called oil of vitriol. $H_2S_2O_7$, then, is the true oil of vitriol. Nordhausen is the town where the acid was formerly made; now it is also made in Bohemia. $H_2S_2O_7$ fumes, and if heated gives off SO_3, becoming H_2SO_4. It resembles H_2SO_4 in its properties, but is more intense in its action. When mixed with H_2O it hisses like red hot iron in H_2O. It dissolves indigo and some other substances that are not dissolved in H_2SO_4. It has a sp. gr. of 1.85. There is only one salt corresponding to $H_2S_2O_7$, *sodic pyrosulphate*, made by heating acid sodic sulphate.

$$2NaHSO_4 = Na_2S_2O_7 + H_2O.$$

The salt, however, cannot be formed directly from $H_2S_2O_7$.

SULPHURIC ANHYDRIDE, SO_3, is most easily obtained by heating $H_2S_2O_7$. It is a volatile solid of the consistency of wax, and crystallizes in long white needles. It hisses in H_2O, combining with it to form H_2SO_4, and consequently attacks the fingers if they are moist.

SODIC HYPOSULPHITE, $Na_2S_2O_3$. (The hydrosulphurous acid, H_2SO_2, is of merely theoretical importance). The hyposulphurous acid, $H_2S_2O_3$, has never been obtained, but the hyposulphites are well defined. They can be made by boiling S with the hydrate of the element whose salt is required.

$$6NaOH + 3S_2 = Na_2S_2O_3 + 2Na_2S_2 + 3H_2O.$$

But the usual way to make $Na_2S_2O_3$ is from the soda waste of Le Blanc's process, which consists chiefly of CaS, but also contains some Na_2CO_3. This waste is allowed to weather in the air, the CaS being converted gradually to CaS_2O_3, and then by action of Na_2CO_3 to $Na_2S_2O_3$. The usual way of testing for a hyposulphite is to add an acid, as H_2SO_4. $H_2S_2O_3$ is first formed, and the liquid remains clear; but soon the $H_2S_2O_3$ breaks up, and S is precipitated.

$$\begin{aligned} Na_2S_2O_3 + H_2SO_4 &= Na_2SO_4 + H_2S_2O_3. \\ &= Na_2SO_4 + H_2O + SO_2 + S. \end{aligned}$$

The hyposulphite is used in photography to dissolve and wash off the AgCl, AgBr, and AgI, thus fixing the picture; also as an antichlor, to remove the last traces of Cl_2 in bleaching, and in metallurgy. There are many compounds of H, O, and S, called thionic or polythionic acids, as $H_2S_2O_6$, dithionic, $H_2S_3O_6$, trithionic, etc.

Carbonic Disulphide, CS_2, is made by burning carbon in sulphur, as CO_2 is made by burning carbon in oxygen. The burning is done in a porcelain tube or in a retort. The tube is partly filled with charcoal, and heated to redness in a furnace. Some roll brimstone is then dropped in, which at once volatilizes, the C burns in the S vapor, and CS_2 passes off. In the retort method a retort is about half filled with charcoal, heated, and then S is dropped in through a hole at the top. CS_2 is formed and distils off through a tube in the side of the retort. CS_2 is a liquid, colorless when pure, has a high index of refraction, and is therefore sometimes used for prisms in the spectroscope. When pure it has a faint aromatic odor, but it usually has a disgusting smell, due to impurities, or to partial decomposition by the O of the air. It has a very low boiling point, 47°, and is very inflammable, burning with a blue flame and forming CO_2 and SO_2. It is somewhat poisonous, and is occasionally used to kill vermin in birdskins and grain. *Uses:* The present important uses of CS_2 depend chiefly on its solvent power; it dissolves gums, fats, essential oils, sulphur and rubber (hence used in vulcanizing rubber), and ordinary phosphorus. A solution of rubber in CS_2 forms a good varnish. It has been proposed to use CS_2 instead of H_2O in boilers; the advantage would be in the saving of fuel, since CS_2 boils so easily. It could also be condensed and used over and over again, and is very cheap, the chief cost being that of the S. CS_2 burns with NO, giving a flame sufficient to take photographs. It is also used in preserving fruit; if a few drops are put into a jar of fruit and the jar tightly sealed, the fruit is said to keep perfectly. CS_2 is the anhydride of an acid, H_2CS_3, corresponding to H_2CO_3; salts of this acid are well defined.

Carbonic Oxysulphide, COS, is prepared by adding H_2SO_4 to KSCN, thus setting free HSCN, which is then decomposed as follows:

$$HSCN + H_2O = NH_3 + COS.$$

COS is a combustible gas, burning with a blue flame, and has a sp. gr. of 30 referred to H. It is found in some mineral springs. It is decomposed by the hydrates of the alkaline metals and of the alkaline earths.

$$BaO_2H_2 + COS = BaCO_3 + H_2S.$$

The presence of the H_2S can be shown by $Pb(C_2H_3O_2)_2$, which is blackened, forming PbS. Since the formation of PbS is the ordinary test for H_2S, and since the precipitation of $BaCO_3$ may be used as a test for CO_2, COS, when first observed, was thought to be a mixture of H_2S and CO_2. When it is in solution in H_2O, it is gradually decomposed, CO_2 and H_2S being evolved.

$$COS + H_2O = CO_2 + H_2S.$$

Sulphur forms several compounds with chlorine, which are all liquid.

Selenium, Se, at. wt. 78, and **Tellurium,** Te, at. wt. 128. Selenium is found in Clausthalite, PbSe, and was discovered by Berzelius in 1817. It often occurs as an impurity in S and FeS_2; consequently it is sometimes obtained from the dust in the flues of H_2SO_4 works. Tellurium was discovered by Klaproth, in 1798, and occurs in considerable quantities in the Western United States. Graphic Tellurium is a rare mineral containing gold, silver, and tellurium, occasionally lead and antimony. Tellurium is also found in a few other scarce minerals. These elements are both very rare, and are important only on account of their relation to S, with which they form a group parallel to the chlorine group. Observe the position in Mendelejeff's table; we have

Cl	35.5	Br	80	I	127
S	32	Se	78	Te	128

Cl yellowish green.	S yellow.
Br red, black in large masses.	Se black, red in powder.
I gray with met. lustre.	Te iron gray.

Each element forms a hydride:

$$\left.\begin{matrix}HCl\\H_2S\end{matrix}\right\}\text{ stable.}\quad\left.\begin{matrix}HBr\\H_2Se\end{matrix}\right\}\text{ less stable.}\quad\left.\begin{matrix}HI\\H_2Te\end{matrix}\right\}\text{ very unstable.}$$

H_2Te is instantly decomposed by air. SeO_2 is a solid less stable than SO_2, and TeO_2 is a solid still less stable. H_2SeO_4, selenic acid, is a liquid, and strongly resembles H_2SO_4. It forms K_2SeO_4, potassic selenate, white. H_2TeO_4, telluric acid, is a solid. Compounds of Se are the worst smelling inorganic substances known. H_2Se smells like rotten horse-radish; a whiff of the pure gas takes away the sense of smell for several days. Compounds of Te are very nearly as bad.

Rarer Elements. Some of these are not so rare as Se and Te, but they are of small importance. *Molybdenum*, Mo, is found in Molybdenite. Ammonic molybdate, $(NH_4)_2MoO_4$, is used as a test for phosphates. *Tungsten*, W, is found in the mineral Wolfram. Most of its salts are white. Calcic tungstate is very heavy. *Uranium*, U, is the element of the highest atomic weight. Its salts are mostly yellow; some of them have a green fluorescence, which they can impart to glass. *Vanadium*, V, forms potassic vanadate, which is a powerful oxidizer. *Niobium*, Nb, and *Tantalum*, Ta, are extremely rare. Niobium was originally called columbium, because found in America. *Titanium*, Ti, is rather less rare. *Zirconium*, Zr, is found in the rare mineral Zircon. Its transparent crystals are sometimes used as precious stones. *Thorium*, Th, is found in Thorite, and is very rare. *Thallium*, Tl, was discovered in 1861 by means of the spectroscope. Besides these there are the elements of the cerium group.

Theoretical Chemistry. DETERMINATION OF ATOMIC WEIGHTS. In determining the atomic weight of an element two classes of data are used, which can come under the general heads of Analysis and Determination of Formula. I. *Analysis*. It is necessary that the percentage of the element in some compound or compounds should be determined. This can be done either by analysis or by synthesis, but is usually done by analysis. The compound used must have the following characteristics: (1) It must be a definite compound. (2) It must be easily purified, and we must be able to tell when it is pure. (3) It must be stable; (4) easily analyzed or synthesized; (5) as simple as possible. The atomic weight can be determined, after the analysis or synthesis, in four ways.

II. *Determination of Formula.* (*a*) ***By comparing the volatile compounds of an element.*** This method consists in taking a large number of the volatile compounds of the element whose atomic weight is sought, and finding the specific gravities of their vapors. From these specific gravities the molecular weights of these volatile compounds are determined. For instance, suppose it be required to find the atomic weight of chlorine. The molecular weights of a large number of volatile compounds of chlorine are obtained, as,

Hydrochloric acid, . . .	mol. wt.	36.5
Arsenious chloride, . . .	" "	181.5
Silicic chloride, ...	" "	170.

By analysis of each substance the percentage of chlorine in each is determined, and from this the weight of chlorine in each molecule. Thus,

Wt. Cl in one mol. hydrochloric acid,	35.5
" " " arsenious chloride,	106.5
" " " silicic chloride,	142.

By comparing these results we see that the smallest amount of chlorine in any one molecule is 35.5, and that the amounts in each of the other molecules are simple multiples of this weight. Since the atom of an element is the smallest amount in any molecule, and since 35.5 is the smallest weight of chlorine that occurs in the range of our observation, we are justified in assuming that hydrochloric acid contains only one atom of chlorine, and that 35.5 is the weight of the chlorine atom. If in future another compound of chlorine be discovered in which the weight of the chlorine is less than 35.5, this atomic weight must be reduced.

(*b*) *By analogy.* In case the element does not form a sufficient number of volatile compounds, it is necessary to determine the atomic weight in some other way. For example, suppose we wish to determine the atomic weight of rubidium. We do not know the formula of the chloride, but we know by analysis that it contains 85 parts rubidium to 35.5 parts chlorine. If, then, its formula be $RbCl$, since the atomic weight of chlorine is 35.5, the atomic weight of rubidium would be 85. If the formula is $RbCl_2$, the weight of chlorine in the molecule would be 71; and since the proportions are 85 parts rubidium to 35.5 parts chlorine, the atomic weight of rubidium would be 2×85, or 170. Similarly, if the formula is $RbCl_3$, the atomic weight of rubidium will be 255. The problem is to find out which formula is correct. Now the element rubidium is found with potassium, and resembles it in many of its properties; it cannot exist in air, takes fire in water, its hydrate is soluble and strongly alkaline; it has both an acid and a neutral sulphate, and its sulphate, like K_2SO_4, forms an alum. Hence it is fair to suppose that its chloride is RbCl, like KCl, and that the atomic weight of rubidium is 85. This method is not absolutely safe; it failed in the case of indium, the oxide of which was supposed to be InO, like ZnO, since indium resembles zinc.

(*c*) *By Specific Heat.* The law of specific heats is called the law of Dulong and Petit. The specific heat of a substance is the amount of heat required to raise a unit of it one degree in temperature, in comparison with the heat required to raise the same weight of water the same amount. Thus, if the heat required to raise one pound of water one degree be reckoned as 1, the amount required for one pound of iron is .1138. The specific heat of nearly all the elements has been determined experimentally, and it is found that the specific heat of each element, multiplied by its atomic weight, gives a quantity which is nearly constant for all the elements, varying only between about 5.7 and 6.9. In this way we can verify the atomic weights obtained by the other methods. For example, if the specific heat times the calculated atomic weight give 12, we know that we have two atoms instead of one, and therefore that we must halve our calculated atomic weight. There are three exceptions to this law, the elements C, Si, and B. These elements resemble each other, each has three modifications, and each modification has a different specific heat. Probably glucinum is another exception to the law. The theoretical explanation of the law is that the atoms of the different elements have the same capacity for heat. If, for example, it requires the same amount of heat to increase by one degree the temperature of one atom of Fe (at. wt. 56), and one atom of Hg (at. wt. 200), it will also require the same to raise 56 lbs. Fe and 200 lbs. Hg one degree, since the two contain the same number of atoms. Therefore 56 × sp ht. Fe must equal 200 × sp. ht. Hg.

(*d*) This is the method which Mendelejeff used in calculating the atomic weight of In. It presupposes that the properties of the element whose atomic weight is required are known, and that Mendelejeff's classification is a true one.

Molecular Weights. In determining the molecular weights of volatile substances, it is necessary only to find the sp. gr. of the substance referred to hydrogen gas. Since by Avogadro's law equal volumes of all gases under like conditions of temperature and pressure contain the same number of molecules, the weight of each molecule of the substance referred to a molecule of H will be equal to the sp. gr. of the substance. But since the H atom is taken as the unit, and the H molecule contains two atoms, the molecular weight of a substance is obtained by multiplying its sp. gr. by 2. The proof that the hydrogen molecule contains two atoms is as follows: If one volume of hydrogen gas be mixed with one volume of chlorine gas, they will unite to form two volumes of hydrochloric acid gas. Since, by Avogadro's law, equal volumes of all gases contain the same number of molecules, the hydrochloric acid formed must contain twice as many molecules as the hydrogen did; and since each atom of hydrochloric acid contains one atom of hydrogen, the hydrogen molecule must contain two atoms. This can be represented graphically thus:

$$\mathrm{H\text{-}H + Cl\text{-}Cl = HCl + HCl.}$$

Avogadro's law applies only to volatile substances. For non-volatile substances, and for a certain class of exceptions to be described below, the molecular weight must be determined in other ways. It is usually done by studying the properties of the substance. For instance, required the molecular weight of ammonic chloride. This salt can be converted into the neutral sulphate, and also into the acid sulphate. The acid sulphate is a stable salt; but only the univalent basic radicals give stable acid sulphates. If ammonium is univalent, the molecular weight of ammonic chloride must correspond to the formula NH_4Cl; for if the formula were $(NH_4)_2Cl_2$, we should have this graphical symbol:

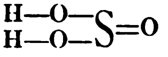
$$\begin{array}{l}\mathrm{Cl—N\equiv H_4}\\ \mathrm{Cl—N\equiv H_4}\end{array}$$

There is nothing to join these parts together, and hence the formula must be NH_4Cl. This reasoning applies to all similar compounds. If the substance of which we wish to find the molecular weight be an acid, we first analyze it to find what the simplest formula would be. For instance, the simplest formula of nitric acid would be HNO_3. Since the acid is found to be monobasic, we infer that in contains only one atom of H, and hence that its formula is HNO_3, and not $H_2N_2O_6$, or some other multiple of HNO_3.

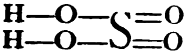
Avogadro's Law. The strongest proof of this law is experimental. The sp. gr. of water vapor referred to H is 9, and hence its molecular weight is 18. Now it has been found by chemical means that the formula of water is H_2O, and that it has 16 parts of oxygen to 2 of hydrogen; and $16+2=18$. *Exceptions to the law.* There are many apparent exceptions to the law, as, for example, NH_4Cl. The molecular weight of NH_4Cl must be the sum of the weights of the atoms, wnich is $14+4+35.5=53.5$. But its vapor density is 13.4, and hence, by Avogadro's law, its molecular weight should equal 26.8, which is only one-half of 53.5. This weight is impossible, for the chloride must contain at least one atom of chlorine, and must therefore weigh over 35.5. The apparent inconsistency is explained by supposing that each molecule of NH_4Cl breaks up on heating into two molecules, NH_3 and HCl. Thus one volume expands into two, and, as the volume is doubled, the sp. gr. is only one-half of what it should be. This theory is called *dissociation*, and explains satisfactorily all exceptions to Avogadro's law. We have no direct evidence that the NH_4Cl really breaks up, but the theory is rendered nearly certain by the action of $N(CH_3)_4I$, which is a solid. Upon heating this substance a liquid distillate is formed, which can be separated by treatment with water into two substances, CH_3I and $N(CH_3)_3$; hence we know that the liquid distillate is a mixture of these substances. On standing they combine to form $N(CH_3)_4I$.

GRAPHIC SYMBOLS. Graphic symbols show the constitutions of substances, that is, the way the atoms unite. The quantivalence of an element probably varies in different compounds, although some chemists maintain that it is always the same. But in the compounds of S, S would seem to be sometimes bivalent, sometimes quadrivalent, and sometimes sexivalent. Thus we have

$H-S-H$

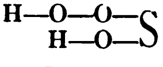


$$\begin{matrix}H-O-\\H-O-\end{matrix}S=O$$



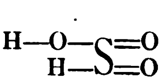
$$\begin{matrix}H-O-\\H-O-\end{matrix}S\begin{matrix}=O\\=O\end{matrix}$$

Those who favor the fixed quantivalence theory, regarding S as always bivalent, would write H_2SO_3 thus:



$$\begin{matrix}H-O-O-\\H-O-\end{matrix}S$$

This is probably incorrect. Besides the above form of H_2SO_3, which makes S quadrivalent, the following form also exists, in which it is sexivalent:



$$\begin{matrix}H-O-\\H-\end{matrix}S\begin{matrix}=O\\=O\end{matrix}$$

This differs from the first in that one atom of H is united directly with the S, while in the other both atoms of H are united to the S by means of O. The combination of atoms H—O— is termed *hydroxyl*. The first symbol, making S quadrivalent, contains two of these combinations, while the second contains but one. All acids which form salts ending in —*ite* and —*ate* are supposed to contain hydroxyl.

Isomeric substances are substances which have the same composition but different constitutions; that is, they differ in the arrangement of atoms in the molecule. In other words, they have the same empirical, but not the same graphical, symbol. For instance, $C_3H_6O_2$ exists in two forms, having different constitutions, as is shown by the fact that upon adding KOH to one, methyl alcohol, CH_3OH, is formed, while by adding KOH to the other form, ethyl alcohol, C_2H_5OH, is formed. The proper way to distinguish between the two forms is to write the formulas $CH_3C_2H_3O_2$ (methyl acetate) and $C_2H_5CHO_2$ (ethyl formiate). The reactions with KOH are

$$CH_3C_2H_3O_2 + KOH = CH_3OH + KC_2H_3O_2.$$
$$C_2H_5CHO_2 + KOH = C_2H_5OH + KCHO_2.$$

H_2SO_3, which exists in two different forms, is another example of isomerism. *Polymeric substances* are substances which have the same simplest formulas, but differ in molecular weights. Thus, CH_2, C_2H_4 and C_3H_6 are polymeric.

Crystalloids are substances which can form crystals. *Colloids* are substances which are of a gluey nature. Crystalloids include nearly all inorganic substances and some organic. Colloids include the higher organic substances and some inorganic substances, as silicic acid.

MENDELEJEFF'S TABLE. As a general rule, compounds of elements which stand in the same series have similar formulas. The exceptions to this rule are, in the first series Au and Cu; in the second series Hg, which is to be connected with Cu in the first series. In the third series there are no important exceptions. In the fourth series the exceptions are Sn and Pb. Pb is closely connected, both in the formulas of its compounds and in properties, with Ba in the second series. In the fifth series there are no exceptions, and P may be taken as a model. In the sixth series Cr forms an exception, and is closely connected with Mn in the seventh. In the formulas of their lower compounds these two elements may be connected with the eighth series and Aluminum. In the seventh series Mn is the only exception.

In going down a series the elements usually become more basic, while in going along a row from left to right they usually become more acid. In the first and second series, however, this is reversed, the stronger bases being near the top. The elements which form colored compounds are mostly those which stand in or near the eighth series. The oxides, sulphides, and iodides, of metals that form any colored compounds, are usually colored.

All oxides of metals are insoluble, except perhaps HgO. All hydrates of metals are insoluble, except those of the alkalies and alkaline earths, and PbO_2H_2, which is slightly soluble. The nitrates are all soluble. The carbonates are all insoluble, except those of the alkaline metals.

ERRATA.

Page 6, line 6 from bottom, read "HYDROCHLORIC."
" 7, " 9, for "gas" read "liquid."
" 7, " 16, for "H" read "O."
" 8, " 22, for "$NaHPO_4$" read "Na_2HPO_4."
" 9, " 22, read, "drastic remedy, for rheumatism, and etc."
" 9, " 9, for "nitrogen" read "hydrogen."
" 9, " 16, for "trough" read "froth."
" 17, " 4, for "quartz" read "granite."
" 17, " 16, for "Prussia" read "Russia."
" 17, " 6 from bottom, for "pinkish" read "bluish."
" 20, " 17, for "bronze" read "oak."
" 20, " 20, omit the words "called edgestones."
" 20, " 23, after "discs" insert "or by toothed wheels."
" 21, heading, for "CALSIUM" read "CAESIUM."
" 23, line 22, for "continuous" read "intermittent."
" 24, " 1, for "Co_2" read "CO_2."
" 95, " 24, 27, and 30, for "CO" read "Co."
" 108, " 22, for "$PbOPb(C_2H_8O_2)_2$,"
read "$PbOPbOPb\ (C_2H_3O_2)_2$."
" 118, reaction, for "3CO" read "$3CO_2$."

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